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# I. GENERAL REVIEW

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Comments on the “ Haute-Nendaz ” Conference

on

## THE MAGNETIC RESONANCE OF DILUTE MAGNETIC ALLOYS

BY

**R. ORBACH \***, **M. PETER \*\*** and **D. SHALTIEL \*\*\***

October, 1973

On September 3, 1973, a Conference on the electron paramagnetic resonance of dilute magnetic alloys was held in Haute-Nendaz, Valais, Switzerland. It was sponsored by the Swiss Academy of Sciences, and involved seventy (70) scientists from nearly every scientifically active country in the world. It was organized by Professors Giovannini and Peter, under the able hands of Miss Zeier, from the Département de Physique de la Matière Condensée, Geneva, Switzerland. A list of participants is contained in this collection of papers submitted by those in attendance. The diverse techniques with which the participants were conversant, and the variety of materials with which they worked, gives evidence of the richness of the subject, and the very considerable amount of physics to be learned. It is hoped that this conference served as a unifying element, enabling a cross-fertilization to enrich the respective research programs.

This “covering” paper, written after the conference had concluded, attempts to put the development of the field into a “personal” perspective. We hope it will give the reader some insight into the significance and promise of papers collected together in this volume. It is certainly not meant as an exhaustive survey. It merely

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attempts to give the reader a "flavor" of the subject which he can use to assess its significance and future direction. First, the historical development of the concepts inherent to an understanding of the subject will be given. Afterwards, a very brief summary of the experimental and theoretical papers which we felt to have been most significant will be presented. We do not mean to imply that by omission we feel other material is not important. Rather, we are attempting to present a very personal view of the subject. It is impossible to include every work of significance. Finally, some speculations about future directions of research in the field of *EPR* in metals is presented, with the full realization that only time will determine which of our guesses were right, and which were foolish.

## I. A CONCEPTUAL HISTORY

The study of Owen, Browne, Knight and Kittel [1] was the first report of paramagnetic resonance of dilute magnetic ions in metallic solid solution. It still remains a useful starting point for a discussion of the development of the concepts involved in this field (interestingly enough, not for what they did observe, but rather for what they did not). Specifically, the experimental results, especially their contradiction with existing theoretical expectations, raised many of the questions which, even today, continue to stimulate both experimental and theoretical studies. Owen *et al.* measured the magnetic resonance spectra of dilute (approximately 1%) *Mn* in a variety of host metals (e.g. *Cu*, *Ag*, *Mg*). They expected to observe a large positive *g* shift, proportional to the *Mn* susceptibility, an enhanced host Knight shift, and the *Mn* fine- and hyperfine-structures so common in ionic hosts. Instead, they observed only a small temperature independent *g* shift, no fine- or hyperfine-structure, and at low temperatures evidence for antiferromagnetic resonance at measurable concentrations. In the ten years that followed, the concepts evolved slowly, permitting finally the rather radical differences between expected and observed behaviour to be reconciled. In addition, the magnetic resonance of a number of *S*- (and, finally in 1966 [2], non *S*-) state impurities in different metallic hosts was reported.

The paper of Hasegawa in 1959 [3] presented the first successful comprehensive treatment of the problem of resonance in dilute magnetic alloys. He recognized that the magnetic impurities were to be considered not as independent agents perturbed only weakly by the host metal conduction electrons, but rather that their respective magnetizations were linked together by the exchange coupling. He hypothesized a pair of coupled Bloch equations for the two fields (localized and conduction electron magnetizations) which today are known as the Hasegawa equations. Curiously, he proposed two versions: in version *A*, the relaxation of the magnetizations took place towards only the averaged (or thermal equilibrium, in the absence of the *rf* field) internal field. In version *B*, relaxation took place towards both the instan-

taneous external *and* internal fields. The self molecular field does not act because it is parallel to the magnetization itself, and hence exerts no torque.

Subsequently, it became clear that relaxation to the instantaneous local molecular field was the only hypothesis which, at least in the limit of small transverse magnetization, leads to dynamic transverse susceptibilities which satisfy the (equivalent) requirements of passivity and causality, or conformity with the dispersion relations [4]. Molecular field equations which obey the dispersion relations for all values of magnetization  $\vec{M}$  can be constructed by introducing relaxation terms with the Landau-Lifshitz form [5]:

$$\begin{aligned} d\vec{M}_i/dt &= g_i u_\beta \{ \vec{M}_i \times (\vec{H} + \lambda_{ie} \vec{M}_e) \} + R_i(\vec{H}, \vec{M}_i, \vec{M}_e); \\ d\vec{M}_e/dt &= g_e u_\beta \{ \vec{M}_e \times (\vec{H} + \lambda_{ei} \vec{M}_i) \} + R_e(\vec{H}, \vec{M}_e, \vec{M}_i); \end{aligned} \quad (1)$$

where

$$\begin{aligned} R_i &= -\delta'_{ie} \vec{M}_i \times \{ \vec{M}_i \times (\vec{H} + \lambda_{ie} \vec{M}_e) \} \\ &\quad + \left( \frac{g_i}{g_e} \right) \delta'_{ei} \vec{M}_e \times \{ \vec{M}_e \times (\vec{H} + \lambda_{ei} \vec{M}_i) \} \\ &\quad - \delta'_{iL} \vec{M}_i \times \{ \vec{M}_i \times (\vec{H} + \lambda_{ie} \vec{M}_e) \}; \\ R_e &= -\delta'_{ei} \vec{M}_e \times \{ \vec{M}_e \times (\vec{H} + \lambda_{ei} \vec{M}_i) \} \\ &\quad + \left( \frac{g_e}{g_i} \right) \delta'_{ie} \vec{M}_i \times \{ \vec{M}_i \times (\vec{H} + \lambda_{ie} \vec{M}_e) \} \\ &\quad - \delta'_{eL} \vec{M}_e \times \{ \vec{M}_e \times (\vec{H} + \lambda_{ei} \vec{M}_i) \}. \end{aligned} \quad (2)$$

The small transverse magnetization limit of (1) and (2) reduces to case *B* of Hasegawa [3]. We have adopted the Geneva group notations in (1) and (2). The subscript *i* refers to the magnetic impurity, *e* to the conduction electrons. The field  $\vec{H}$  includes both static and dynamic (transverse *rf*) fields. The internal exchange fields are defined by  $\lambda_{ie} = J/g_i g_e$ , where *J* is the localized conduction electron exchange integral (see Section III, eq. 15), and the relaxation constants,  $\delta'_{ie}$ ,  $\delta'_{ei}$ ,  $\delta'_{eL}$ ,  $\delta'_{iL}$ , are primed because of their usual definition in the small transverse amplitude limit:

$$M_e^z (H^z + \lambda_{ie} M_e^z) \delta'_{ie} = \delta'_{eL} \quad ; \quad M_i^z (H^z + \lambda_{ie} M_e^z) \delta'_{iL} = \delta'_{iL}. \quad (3)$$

Defining  $M^\pm = M_x \pm iM_y$ , (3) allows (2) to be written as ( $\lambda_{ie} = \lambda_{ei}$ )

$$\begin{aligned} R_i^\pm &= -\delta_{ie} (M_i^\pm - \chi_i \lambda_{ie} M_e^\pm) \\ &\quad + \left( \frac{g_i}{g_e} \right) \delta_{ei} (M_e^\pm - \chi_e \lambda_{ie} M_i^\pm) \\ &\quad - \delta_{iL} \{ M_i^\pm - \chi_i (M^\pm + \lambda_{ie} M_e^\pm) \} \end{aligned} \quad (4)$$

with an equivalent expression for  $R_e^\pm$  obtained upon interchange of *i* and *e* subscripts. Use of (4) in (1) allows one to obtain the dynamic transverse response.



The major conclusions to be drawn from the molecular field equation is the appearance of "bottlenecking" whenever the transfer of magnetization from the magnetic impurities (conduction electrons) to the conduction electrons (magnetic impurities) is faster than the transfer of magnetization from the magnetic impurities (conduction electrons) to the lattice. Under such circumstances, the magnetic impurities and conduction electrons act as a firmly locked entity whose  $g$  value and line width are given by the susceptibility weighted average of the impurity and conduction electron  $g$  value and lattice line width. The first systematic bottleneck study was carried out by Gossard, Heeger and Wernick [6] (see also Gossard, Kometany and Wernick [7]), with the essential theory for conduction electron-lattice spin flip relaxation given by Yafet [8]. The bottleneck condition was altered by the addition of non-magnetic impurities, whose spin-orbit coupling caused an increase in the lattice relaxation rate of the conduction electron magnetization. A similar mechanism for the localized spins, proposed by McElroy and Heeger [9], has now been shown to be wrong [10].

Apparently, in transition metal hosts, where the  $d$ - or  $f$ -band is sufficiently narrow, the lattice relaxation rate of the conduction electrons either due to phonons or through residual impurities (the relaxation rate is proportional to the host density of states squared through the quadratic dependence on the virtual level width) is sufficiently great to break the bottleneck. The system  $Pd:Gd$  allows one to test the validity of the molecular field equations in several ways. The proportionality of the  $g$  shift to the host metal conduction electron polarization was verified by:

- a) varying the conduction electron susceptibility  $\chi_e$  by adding  $Rh$  and  $Ag$  to  $Pd$  [11];
- b) varying the conduction electron polarization directly by addition of other (magnetic) rare earth impurities [12].

The latter experiments (because of the observation of a  $g$  shift) showed incidentally that  $Pd$  is a host in which the polarization about a magnetic impurity has an unusually long range [13]. This is caused by the large  $\vec{q} = 0$  exchange enhancement of the conduction electron susceptibility.

The reasons for the remarkable success of the molecular field picture are by no means obvious. For example, the static polarization around the magnetic impurity is far from uniform (by virtue of the Ruderman-Kittel oscillations). The structure of the microscopic theories which emerged in the latter half of the 1960's [14] showed that the dynamic polarization on or near resonance is of very large effective range. It is this feature which makes the molecular field such a good approximation. The argument is as follows: If the  $g$  factors of the magnetic impurities and the conduction electrons are very close, only the  $\vec{q} \cong 0$  spin wave mode of the conduction electrons will be resonant with the magnetic impurities. That is, modes with  $1/|\vec{q}| < \text{Fermi velocity}/\text{Zeeman frequency}$  are not resonant, so that the electron

spin sublattice which couples to the ions is effectively rigid over a range  $10^8 / 10^{10} = 10^{-2} \text{ cm}$ . If  $g_i \neq g_e$ , coupling will occur for progressively larger values of  $\vec{q}$ , and leads to larger couplings of non-uniform conduction electron spin waves. However, at concentrations accessible in the laboratory, these terms will never be important for reasonable values of  $g_i$ .

The microscopic theories mentioned so far have all used a very simplified parametrization of the magnetic impurity-conduction electron interaction : the free ion effective exchange

$$- (J/N) \sum_i \vec{S}_i \cdot \vec{s}_e(\vec{r}) \delta(\vec{r} - \vec{R}_i) \quad (5)$$

where  $\vec{r}$  is the position coordinate of the conduction electron, and  $\vec{R}_i$  that of the magnetic impurity. This ferromagnetic coupling ( $J$  positive) [15] was originally believed to represent the situation in dilute alloys. However, the early magnetic resonance observations in some hosts of a negative  $g$  shift, hence an antiferromagnetic sign of the interaction parameter ( $J$  negative), showed that another mechanism besides atomic exchange must be present. Though this has been used to justify the inter-band mixing mechanism of Anderson and Clogston [16], and Kondo [17], it now appears that for non-orthogonal orbitals in the theory of super-exchange [18] it is also negative [19]. Nevertheless, the interband mixing mechanism is recognized to be dominant for the rare earths *Ce* and *Yb* (when in the magnetic state) and for most transition metal impurities.

This contribution was elegantly exhibited in Anderson's theory for a localized moment in a metal [20]. A direct relationship between the admixture model, and the "ionic" form for the exchange (displayed above) was developed using a simple linear transformation by Schrieffer and Wolff [21]. Letting the admixture Hamiltonian have strength  $V_{sd}$ , the effective exchange coupling equals

$$J = - V_{sd}^2 \left[ \frac{1}{E_d^+} + \frac{1}{E_d^-} \right] \quad (6)$$

where  $E_d^+$  and  $E_d^-$  refer to the energies (relative to the Fermi surface) of the virtual  $d$  levels for up and down spin directions. For full magnetization, they differ in energy by the coulomb repulsion  $U$  (usually estimated to be of the order of  $10 \text{ eV}$ ). For  $V_{sd} \sim 1 \text{ eV}$ , and the terms in the parenthesis of the order of  $\sim 0.2 \text{ eV}^{-1}$ , one finds an effective (negative) exchange of  $- 0.2 \text{ eV}$ . This is nearly equal to values recently obtained for *Cu:Mn* by *NMR* techniques [22].

Yet another contribution to the effective exchange coupling was presented by Salamon [23]. He argued that the  $5d$ -like screening electrons via inter-band mixing couple (negatively) to the conduction electrons. The (positive)  $5d$  exchange coupling with the occupied  $4f$  electrons then leads to an effective negative localized-conduction electron exchange interaction. The anisotropic host susceptibility of hexagonal *Sc*

then results in an anisotropic  $g$  shift for  $Sc:Gd$ , and could account for the anisotropy of the linewidth and field for resonance of this alloy (but see the discussion in Section II on crystal fields in dilute alloys).

A very large amount of theoretical and experimental work has been based on, and interpreted in terms of, the "local" exchange interaction (5). Such quantities as the Curie temperature, superconducting transition temperature, and residual resistivity are related to  $J^2 N(E_F) S(S+1)$ , where  $N(E_F)$  is the density of conduction electron states at the Fermi energy, and  $S$  the magnitude of the magnetic impurity spin. Once  $N(E_F)$  is known,  $J^2$  can be determined. The quantities such as the  $g$  shift, the paramagnetic and ferromagnetic moment, and the Kondo temperature, are related to  $JN(E_F)$ . Once  $N(E_F)$  is known, one can derive both the magnitude and sign of  $J$ . A single measurement, that of the influence of the exchange field or the so-called Pauli term for the upper critical field for magnetic superconductors, gives  $J < S >$  directly, thereby determining  $J$  without the requirement of knowing  $N(E_F)$ .

One interesting endeavour is to measure several of these quantities in the same substance, and to look for consistency [24]. This has been done, for example, by Devine *et al.* [25] for  $Mn$  in  $Mo_7Ga_{31}$ . On this occasion, the results were nearly as different from expectations as were those of Owen *et al.* 14 years earlier. Studies of  $H_{c2}$  vs concentration of  $Mn$  gave  $J = -0.34$  eV. However, the  $EPR$   $g$ -shift was distinctly positive, and strongly temperature dependent. One is forced to admit that the field of the  $Mn$  ions on the superconducting electrons is quite different from the field which the conduction electrons exert on the  $Mn$  ions. This implies that not all conduction electrons, but only one of the bands or even sub-bands, participates in superconductivity [26]. The highly paramagnetic sub-band may be different from the sub-band principally responsible for conductivity. And, each may possess its own coupling to the magnetic impurities. The strong temperature dependence of the  $g$  shift (and line width slope) may be ascribed to the interposition of a loosely bound (narrow, quasi-localized) state between conduction electrons and localized moments.

The incompatibility of magnitudes, and even signs, of  $J$  as deduced from different measurements should motivate future work in the field of  $EPR$  in metals. Also the time is long overdue for the conduction electrons to be introduced into the picture using the correct host band structure.

Further progress towards realism will be achieved when crystal fields are reasonably understood. The effects of crystal field splittings on both  $S$ -state and non  $S$ -state ions have been observed experimentally only recently. Several difficulties had to be overcome. First, sufficient spectrometer sensitivity had to be achieved (in practice, reduced background) so that observation of  $EPR$  in highly diluted single crystals could become possible. Second, the importance of hopping between crystal field split Zeeman levels (for  $S$ -state ions) caused by impurity-conduction electron mutual spin flips had to be recognized, and calculated. Detailed computations [27]

explained the hitherto puzzling fact that crystal field splittings could only be seen at quite low temperatures and at very low dilutions.

Crystal field parameters have since been obtained for a number of metallic and intermetallic compound hosts [28]. At first sight, in some series, it appeared that the crystal fields so obtained varied quite drastically from one ion to another in the same host [29] and from one host to another for the same ion. Recently, work by Yang *et al.* [30] has led to yet another generalization: the exchange interaction has to be given a more general form than the scalar one of (5) (see section III). The more general form alters the  $g$  value anisotropy from that expected from crystal fields alone, and results in a re-evaluation of the crystal field parameters.

An early study of the interaction between the impurity magnetization and the conduction electrons by Koide and Peter [31] had already exhibited the presence of anisotropic terms. This work was followed by that of Coqblin and Schrieffer [32] which treated the problem of resonant states. Giovannini [33] has recently shown that the anomalous Hall effect would be particularly sensitive to these anisotropies. However, the inclusion of these terms in the spin-Hamiltonian opens truly new and exciting possibilities. The most accurate and direct determination of exchange parameters may well come from *EPR*.

Already, in fact, such a generalization has allowed, for the first time, an acceptable fit of the previously anomalous gamma-8 spectrum of  $Pd:Dy$  [30]. As a result, crystal field parameters for  $Pd:Dy$  and for other  $Pd$  based rare earth alloys now exhibit a smooth variation across the rare earth series. And, explicit values have been obtained for the anisotropic exchange parameters. Similar results have been obtained by Davidov *et al.* [28] for a variety of intermetallic compound hosts.

The basis of the desire for systematics lies in the wish to calculate crystal fields from first principles. Some researchers feel that point charge calculations will work less badly in metals than they do in insulators [34]. Perhaps there is more hope in atomic calculations which amount to band calculations for the host surrounding the magnetic impurity. Some work by Freeman, Watson and Peter is in progress in this direction.

While the path for the understanding of rare earth impurities in metallic hosts is thus reasonably apparent, the situation is much less clear for the case of magnetic transition element impurities. No resolved fine structure or even hyperfine structure has yet been seen in *EPR*. L. Hirst, in a provocative paper [35], has proposed that a crystal field-“ionic” model will suffice to explain the hyperfine field across the  $3d$  series in, for example, copper. If he is correct, it implies that at sufficiently low temperatures and concentrations there should be resolved spectra for  $S$  and non- $S$  state transition impurities (recognizing of course that the exchange relaxation rates all saturate as soon as one is at temperatures lower than the Zeeman energy). Clearly, Hirst’s approach is correct for low conduction electron concentrations (e.g. semiconductor hosts [36]) now experimentally accessible. Whether it is also valid for

dense metals will be ultimately decided by the experimentalists. A better test of the range of validity might be obtained by a re-evaluation of the Anderson model with explicit inclusion of intermediate strength crystal fields.

One severe challenge must be mentioned which hangs over all these calculations: the Kondo effect. It raises its head in all perturbative calculations and should lead to very interesting observable effects in suitably chosen systems. The preceding observations on the necessity of including crystal fields, anisotropic exchange, multiband structure, magnetic resonance bottleneck, and line hopping are all applicable to Kondo calculations in realistic situations. The theory, especially as formulated by Götze *et al.* [22], may someday be generalized to yield predictions for the magnetic resonance and other properties of real magnetic systems to test for the existence of the Kondo effect.

To conclude this section, we list once more the concepts which successively took on importance for the understanding of *EPR* in dilute magnetic alloys:

1.  $g$  shift, thermal line broadening
2. Ruderman-Kittel oscillations
3. Molecular field equations
4. Magnetic resonance bottleneck
5. Dispersion relations
6. Perturbative statistical models based on  $-J\vec{S} \cdot \vec{s}$  exchange
7. Self-consistent Anderson model
8. Multiple bands and sub-bands
9. Loosely bound states
10. Crystal field splittings
11. Line hopping
12. Anisotropic exchange
13. Kondo effect

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## II. SUMMARY OF EXPERIMENTAL DEVELOPMENTS

In the preceding section (I) an overview of the concepts essential to an understanding of *EPR* in dilute magnetic alloys was presented. In this section, we shall concentrate on the development of experimental techniques in this field, with special emphasis on the characteristics of the host metals, and their influence on the magnetic impurities. In fact, the use of dilute alloys as a tool for investigating the electric and magnetic properties of the pure host metal has been slow to develop. The reasons for such slow progress have already been outlined in I: (a) difficulties in realizing the concepts; (b) experimental difficulties in materials preparation, such as making



pure samples and growing single crystals; and (c) detecting the relatively weak signals due to the electromagnetic skin effect.

Table I outlines the historical development of the subject from the experimental point of view.

In the molecular field approximation, the exchange interaction  $-J\vec{S}\cdot\vec{s}$  should produce an additional internal field on the magnetic ion, resulting in a shift of the field for resonance, proportional to the magnetic field.  $J$  is the exchange interaction constant, and  $\vec{S}$  and  $\vec{s}$  the spins of the magnetic impurities and conduction electrons, respectively. The  $g$  shift in the absence of a bottleneck is explicitly given as [3]:

$$\delta g_0 = JN(E_F)/(1-\alpha), \quad (7)$$

where  $N(E_F)$  is the one spin density of states of the conduction electrons. The same interaction produces relaxation of the magnetic impurity spin to the conduction electron spin, and a concomitant broadening (in the absence of a bottleneck)  $\delta H_0$  of the resonance line proportional to the temperature:

$$\delta H_0 = \frac{\pi}{g\mu_B} [JN(E_F)]^2 k_B T \frac{K(\alpha)}{(1-\alpha)^2}. \quad (8)$$

Here, and in (7),  $(1-\alpha)$  is the Stoner enhancement factor for the static longitudinal susceptibility, and  $K(\alpha)$  is a function given by Narath and Weaver [37]. We work in the real spin space, appropriate to  $S$ -state ions. The modifications for effective spin is to replace  $J$  by  $\frac{g(g_J-1)}{g_J} J$ , where  $g_J$  is the Landé factor.

As stated in Section I, the  $g$  shifts and line widths measured by Owen *et al.* [1] for  $Cu:Mn$ ,  $Ag:Mn$  and  $Mg:Mn$  were much smaller than those calculated on the basis of a reasonable value for the exchange constant  $J$  between the  $Mn$  3d and 4s electrons [22]. Further, none of the usual features of the *EPR* in insulators, such as fine or hyperfine structure, was observed. These results were puzzling at the time, although it now seems that it is possible to explain the negligible  $g$  shifts and line widths by virtue of the Hasegawa bottleneck theory [3], and the non-observation of the fine or hyperfine structure from the Barnes-Orbach-Plefka hopping theory [27, 28]. However, development did take place by virtue of an accumulation of experimental evidence: the observation of large  $g$  shifts for  $S$ -state ions  $Gd$  [11] and  $Mn$  [39] in metals, and the correlation between the  $g$  shift and magnetic susceptibility of the host metal. This brought positive new results to the field. New experimental work in powders could be done after the realization that it was possible to observe not only  $S$ -state impurities, but also non  $S$ -state impurities with isotropic ground states (e.g.  $Ag:Er$  [2]). In non- $S$ -state alloys, the hyperfine splitting was observed [40], giving additional information through the hyperfine field about the interaction of the magnetic impurity with the conduction electrons [41]. The system-

atic investigation of the relation between the  $g$  shift and thermal broadening in various systems has clarified the bottleneck problem [6, 7, 42]. The observation of the resonance of single crystals has allowed the observation of (a) the anisotropic doublet spectrum in a non-cubic host [43], (b) the fine structure for  $S$ -state impurities [44, 45, 46], and (c) the non- $S$ -state  $\Gamma_8$  ground state [47, 48].

In what follows, a brief review of the experimental techniques and materials preparation will be given. Then, the  $EPR$  properties, including fine structure, of  $S$ -state ions in unbottlenecked and bottlenecked systems will be discussed. This will be followed by a discussion of non  $S$ -state ions, and a summary of the results of magnetic resonance impurities in pure metals. Some results of  $EPR$  in various hosts (e.g. intermetallic compounds) will be described.

## IIa. Spectrometers

For  $EPR$  of dilute magnetic impurities in metals, it is essential to use an extremely sensitive spectrometer with a temperature control from pumped  $He$  to 50 K. In some cases (especially in more concentrated materials) higher temperatures (even room temperature) may be needed because of interaction effects.  $EPR$  lines are usually broad, of the order of 100 G or more, and large modulation amplitudes may be necessary.

The minimum concentration of impurities,  $c_{\min}$ , that can be detected with a signal to noise ratio  $S$  using a spectrometer of sensitivity  $N_{\min}$  [49] is given by the equation

$$N_{\min} = \frac{c_{\min} A \delta N_V H_m}{(\delta H)^2 S}. \quad (9)$$

Here,  $A$  is the area of the sample ( $0.5 \text{ cm}^2$ ),  $\delta$  the skin depth (1 micron at  $X$ -band),  $N_V$  the number of atoms/ $\text{cm}^3$  ( $5 \times 10^{21}$ ),  $H_m$  the modulation amplitude (30 G),  $\delta H$  the line width (100 G), and  $S$  the required signal to noise ratio (10). Using the numbers written in the parenthesis, one obtains

$$N_{\min} \sim 10^{10} \text{ for } S = 10 \text{ and } c_{\min} = 10^{-3}. \quad (10)$$

Commercial spectrometers can be purchased with  $N_{\min}$  of  $10^{11}$  at room temperature. Such spectrometers should have a sensitivity of  $N_{\min} = 10^9$  at 4.2 K because of the  $(1/T)$  Boltzman factor, and the increase of the  $Q$  of the cavity (if the cavity is at  $He$  temperature). However, this sensitivity is not usually achieved because of the bubbling of the refrigerating liquid. With powders, the signal can be increased by a factor of ten because of the increase of surface area of the sample. It is essential to have a good temperature control system with a reliable thermometer. For the  $He$  temperature region, one can use the  $He$  vapor pressure to measure the temperature. Usually, it is advisable to prevent the liquid  $He$  from going into the cavity to avoid additional noise caused by bubbling. In this case, it is very important to

assure good thermal contact with the *He* bath. Excessive modulation amplitudes may introduce overheating of the sample because of eddy current losses, and lead therefore to erroneous temperature measurement.

Background signals in the cavity are very cumbersome and are observed in most cavities when cooled to liquid helium temperatures. Walsh [50] has produced a very clean cavity made from very pure aluminium-5% magnesium alloy, using very clean dyes.  $TE_{011}$  cylindrical cavities with a finger dewar, whose tip is made of very pure quartz, are most advisable. This arrangement has the advantage of the cavity itself being at room temperature, thereby reducing the background signal to insignificance. The cold finger dewar is very convenient for the use of *He* temperatures. The sample is in direct contact with the liquid, and it is possible to change samples while the dewar contains liquid *He*. Recently, Rettori *et al.* [51] adapted the cold finger dewar for use with  $He^3$  down to 0.5 K.

Signal averaging schemes may be used to enhance the signal-to-noise ratio. It is possible to use multichannel analyzers for this purpose. Recently, microcomputers have been introduced. One microcomputer can serve several apparatuses. In addition to averaging, it can perform useful operations such as differentiation and integration, and more importantly subtraction of background signals (such as linear background due to modulation). It has the additional advantage of recording the signal digitally, which can then be fed to a computer for line shape analysis.

In the early stages of *EPR* in metals, most of the work was done at high frequencies,  $\sim 50$  Gcs [11]. It was believed that, because the shift in resonance field was proportional to frequency (and hence to field), the higher the frequency the better the *g* shift measurement accuracy. This reasoning appears obvious on the surface. However, it was found that the extrapolated residual line width was proportional to frequency, and its contribution to the total line width, even at *X* band, is in most cases comparable to the thermal contribution (8) at 4.2 K. This indicates that at low temperatures one should try to use a low frequency spectrometer. *X* band spectrometers appear to be the optimum available, taking sensitivity considerations into account. With the very rapid development of microwave marginal spectrometers [52] with fairly good sensitivity, one may expect that even lower frequency *EPR* spectrometers may soon be in use. This does not mean that measurements at higher frequencies should be ignored. There are many conceivable situations where two measuring frequencies are needed to be sure of the identification of the correct spin-Hamiltonian.

Two cavity transmission electron spin resonance (*TESR*) spectrometers are also used to observe the *EPR* of dilute magnetic alloys. Gehman and Schultz [54] have observed the *TESR* of *Ag:Er*, but the mechanism which allows for the transmission of the signal is not yet uniquely determined. A different approach is to investigate the shift of the *TESR* line caused by the bottlenecked interaction of the local moments with the conduction electrons [55]. Monod *et al.* [56] have recently



observed *TESR* of a thin foil of *Cu* implanted with *Mn* on either one or both sides of the sample. An increase of intensity over that of the pure *Cu* foil by a factor of 50 per side (2,500 for both sides) was found at 1.5 K. Similar enhancements were found when ferromagnetic films were superposed on a thin metal foil at the magnetic field angle where the ferromagnetic resonance and *TESR* resonance coincide [57]. It is hoped that this new technique will enable *TESR* to be observed in metals where straight *TESR* is not now feasible (because of rapid spin lattice relaxation, for example), and so increase substantially the scope of this method.

### *I Ib. Sample preparation*

It is crucial to use clean and well prepared samples to obtain fruitful results for *EPR* in metals. Many times even the purest, commercially available, metals are not clean enough for *EPR* purposes (especially *TESR*). In preparing alloys, arc furnaces are widely used, and can produce fairly clean samples. Induction furnaces, with water cooled boats, are good too. The use of levitation in induction furnaces results in less contamination than using crucibles. Recently, extremely significant results have been obtained with single crystals, and their importance will surely increase in future research. The literature [58] on growing single metal crystals by conventional methods, such as pulling or zone refining, should be consulted. Many times 50 grams of starting material may be needed to grow a single crystal, and often the sample cut from the boule may weigh only one gram. Taking into account that several concentrations may be needed to investigate any given system, especially if a bottleneck is present, single crystal experiments can be very expensive.

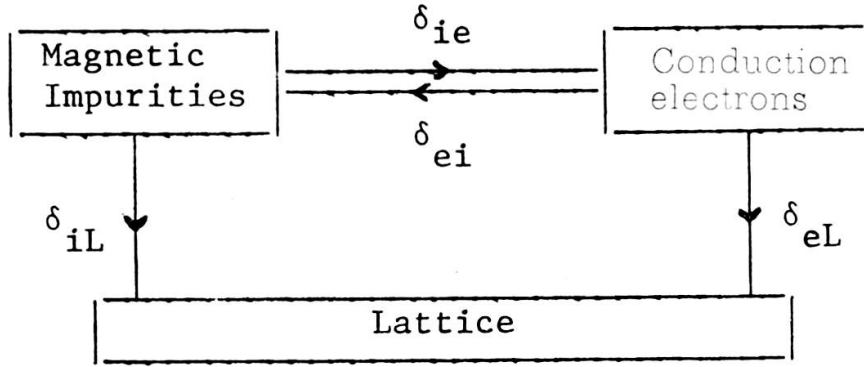
There are some crystal growing methods, such as re-crystallization, where much smaller quantities of metal are needed, and where the final shape will be suitable for measurement. This method has been used in the investigation of *Pd* single crystals doped with rare earth impurities [46, 48].

### *I Ic. Experimental Results*

It is proper to discuss separately *EPR* for *S*-state and non *S*-state magnetic impurities in metals. *S*-state impurities may form bottlenecked systems, and therefore their *ESR* properties may depend strongly on concentration and temperature. Non *S*-state impurities are less affected by the bottleneck (in fact, no bottleneck has been observed, as of this writing).

#### *1. S-state impurities*

The interaction between the localized moments and the conduction electrons, and their interaction with the lattice, is usually represented by the following "flow chart":



Here,  $\delta$  is a relaxation rate, and  $e$ ,  $i$  and  $L$  stand for the electrons, magnetic impurities, and lattice, respectively. The order of the subscripts denotes the relaxation direction (flow of magnetization). The transverse dynamic response of this coupled system has been investigated theoretically by Hasegawa [3] using macroscopic Bloch-type equations for the two spin species (magnetic impurities and conduction electrons). He analyzed two kinds of relaxation terms. In his “case  $A$ ”, relaxation was towards the equilibrium or static external field direction. In his “case  $B$ ”, relaxation was towards the instantaneous internal field. His results for case  $B$ , assuming equal  $g$  factors for convenience, are:

$$\delta g = \delta g_0 \frac{(\delta_{eL})^2}{(\lambda\gamma\chi_i H)^2 + (\delta_{eL} + \delta_{ei})^2} \quad (11)$$

and

$$\delta H = \delta H_0 \frac{[\delta_{ei}^2 + (\lambda\gamma\chi_i H)^2](\delta_{eL}/\delta_{ei}) + \delta_{eL}^2}{(\lambda\gamma\chi_i H)^2 + (\delta_{eL} + \delta_{ei})^2} \quad (12)$$

They are exhibited as a function of the bottleneck parameter  $\delta_{eL} / \delta_{ei}$  in his Fig. 3. Here,  $\gamma$  is the gyromagnetic ratio,  $\lambda$  the molecular field constant (equal to  $J/g_i g_e$ ), and  $\chi_i$  the static susceptibility of the magnetic impurities. The term containing  $H$  is the source of the “dynamic effect” (see below) while  $\delta g_0$  and  $\delta H_0$  are given by (7) and (8), respectively. It has been assumed that  $\delta_{iL} \ll \delta_{ei}$ ,  $\delta_{eL}$ , or  $\delta_{ie}$  (i.e. the direct lattice relaxation rate of the magnetic impurity to the lattice has been taken smaller than all the other relaxation rates. Experimentally, this appears to be a valid assumption). The relaxation rates,  $\delta_{ie}$  and  $\delta_{ei}$ , are related by the detailed balance condition  $\chi_i \delta_{ie} = \chi_e \delta_{ei}$  [3, 59]. For the extreme situation of  $\delta_{eL} \gg \delta_{ei}$ , the  $g$  shift is maximal and equal to  $\delta g_0$  as given by (7). In this limit, the conduction electron spins are relaxing so rapidly to the lattice that all their phase memory is lost. Therefore, they become a polarizeable “bath” and present to the magnetic impurities only their average longitudinal equilibrium magnetization. The linewidth in this limit is given by (8). At the other extreme, when  $\delta_{eL} \ll \delta_{ei}$ , both the  $g$  shift and thermal linewidth tend to zero. The magnetic impurity and conduction electron spins are strongly coupled, and cannot exert a torque on one another. This is the bottleneck limit. Quantum mechanically, for equal  $g$  factors and no lattice damping,

the Zeeman and exchange Hamiltonians commute so that the latter cannot alter the values of the former ( $g$  shift and linewidth).

Before discussing bottlenecked systems, and the methods available for breaking them, it is convenient to discuss examples of unbottlenecked  $S$ -state systems. In such systems, the  $g$  shift is given by (7), proportional to the band density of states, or, more accurately, the  $\vec{q} = 0$  component of the host susceptibility. The  $EPR$  of dilute concentrations of  $Gd$  in the high susceptibility metals  $Pd$  [5],  $LaRu_2$  [60] and  $LaNi_5$  [61] has shown that these systems are not bottlenecked.

Peter *et al.* [11] measured the  $EPR$  of 3%  $Pd:Gd$ ,  $Ag_xPd_{1-x}:Gd$ , and  $Rh_xPd_{1-x}:Gd$  alloys (Fig. 4 of ref. 11). This was the first system to exhibit a clear relationship between the  $g$  shift and the host susceptibility. However, a closer look at their results shows that no linear relation is present between the two, as would be expected on the basis of (7). For example, the susceptibility increases by a factor of two (at 20 K) as  $x$  increases from 0 to 0.05 in  $Rh_xPd_{1-x}$ . However, the  $g$  shift changes from  $-0.1$  to  $-0.11$ , or by only about 10%. The solution to this puzzle was proposed by Cottet and Peter [62]. They noted that a linear relationship is present if one compares the  $g$  shift at low temperatures with the high temperature host susceptibility. They divided the host susceptibility into a long range, non-localized, part (dominant at high temperatures), and an additional short range, localized part (dominant at low temperatures). The latter must assuredly not affect the  $g$  value (it can only increase the line width). Hence, comparison with the former is appropriate. Cottet and Peter also found the  $g$  shift to be concentration dependent, the extrapolated (zero concentration)  $g$  shift was  $-0.22$  in pure  $Pd$ .

If one takes the extrapolated  $g$  shift, and uses the Korringa relation to compute the thermal width (using the results of specific heat, susceptibility, and  $NMR$  to determine  $\alpha$ , and thence  $K(\alpha)$ ), a value is found which is larger by a factor of five than the experimental result. This discrepancy is thought to be due to the wave vector dependence of the exchange coupling [24]. A full discussion will be found in Section III.

The Knight shift of the host metal (in the absence of magnetic impurities), and the  $g$  shift of the impurity, are both proportional to the susceptibility of the host metal, provided the system is not bottlenecked. Therefore, a measurement of  $g$  shift and Knight shift in an alloy where the susceptibility of the host metal can be varied provides a check on the validity of the  $g$  shift theory in metals. This was carried out in the  $La_xTh_{1-x}Ru_2:Gd$  system [63]. Both  $LaRu_2$  and  $ThRu_2$  are superconductors, but  $La_{0.5}Th_{0.5}Ru_2$  is not a superconductor above 1 K. The host susceptibility varies with  $x$ , reaching a minimum at equal mixture ( $x = 0.5$ ). The concentration ( $x$ ) dependence of the  $g$  shift in a 3%  $Gd$  alloy, and the Knight shift of  $La$  in this system, is exhibited in Figure 2 of Reference 63. There is a clear, quantitative, linear relation between the  $g$  shift and the Knight shift, as expected in an unbottlenecked system. The minimum of both quantities at equal mixture ( $x = 0.5$ ) is dramatic.

Because the condition for a bottleneck is given by the inequality  $\delta_{eL} \ll \delta_{ei}$ , it is possible to open the bottleneck by either decreasing  $\delta_{ei}$  or increasing  $\delta_{eL}$ .  $\chi_e$  and  $\delta_{ie}$  (given by (8)) are independent of concentration. Using detailed balance [3, 59],  $\delta_{ei} = \delta_{ie}\chi_i/\chi_e$ , so that  $\delta_{ei}$  is proportional to the concentration through  $\chi_i$ , and can be decreased by decreasing the concentration of the magnetic impurity (explicit expressions for  $\delta_{ei}$  and  $\delta_{ie}$  are given in Section III). Because  $\delta_{ie}$  is proportional to  $kT$  and  $\chi_i$  is inversely proportional  $kT$ ,  $\delta_{ei}$  is temperature independent. Therefore, if  $\delta_{eL}$  is independent of temperature (as it usually is below the temperature where phonon effects become important, typically  $T < 40\text{ K}$ ) the bottleneck strength is independent of temperature. (At very low concentrations,  $\delta_{ie} \gtrsim \delta_{ei}$ , and this is no longer true).  $\delta_{eL}$  can be increased by adding impurities to the host metal that have large spinflip cross sections. The magnetic impurity itself may sometimes spin flip efficiently, and therefore may be the main contributor to the relaxation rate  $\delta_{eL}$ . In such a case, the bottleneck strength parameter,  $\delta_{eL}/\delta_{ei}$ , will remain constant as the magnetic impurity concentration is changed.

Several experiments to remove the bottleneck were made in bottlenecked systems. The first experiments were done in  $\text{Cu:Mn}$  [6] where various additional impurities were added. In these experiments, it was possible to increase the thermal slope of the linewidth, but not the  $g$  value. This follows from the linear dependence on the bottleneck parameter of the former, and the quadratic dependence of the latter (see (11) and (12)). Weimann *et al.* [64] were able to remove the bottleneck of both quantities by decreasing the  $Gd$  concentration in  $YAg$  from 2% to 0.5%. They showed that the functional dependence between the  $g$  shift and the thermal line width was in agreement with Hasegawa's expressions (11) and (12). They also showed that the  $Gd$  contribution to the lattice relaxation rate of the conduction electron spins,  $\delta_{eL}$ , was negligible. Such experiments allow for the quantitative determination of  $\delta_{eL}$  and  $\delta_{ei}$ , provided  $\delta_{ie}$  is known. In  $YAg$ ,  $\delta_{ie}$  derived from the resonance linewidth was a factor of ten smaller than that derived from the  $g$  shift via the Korringa relation. Therefore,  $\delta_{eL}$  and  $\delta_{ei}$  could not be explicitly obtained. The use of a very small  $K(\alpha)$  to account for this difference does not seem justified for this host, and the source of the difficulty undoubtedly lies in the wave vector dependence of the exchange [24].

$Eu$  and  $Gd$  in  $LaAl_2$  are further examples where the bottleneck has been opened by decreasing the magnetic impurity concentration. In this compound, it was possible to obtain numerical values for the exchange constants and the various relaxation rates [65, 66].

Schmidt *et al.* [67] have shown that  $Eu$  in  $Yb$  is a strong spinflip scatterer by varying the  $Eu$  concentration and demonstrating that the bottleneck parameter was unchanged. However, the bottleneck was opened by keeping the  $Eu$  concentration fixed and adding a non-magnetic spinflip scatterer (in this case  $Ca$ ).

The Hasegawa equation for the  $g$  shift, (11), contains the term  $(\lambda\gamma\chi_i H)^2$  in

the denominator. This gives rise to the so-called "dynamic effect". It is proportional to the square of the external field, and at usual concentrations at low temperatures comparable in magnitude with the other terms in the denominator of (11). Davidov and Shaltiel [61] have shown that this additional term accounts for the field and concentration dependence of the  $g$  shift of  $LaNi_5$ . Weimann *et al.* [42] were unable to observe its presence for  $Gd$  in  $YAl_2$  (for unknown reasons), but it has been observed by Schmidt *et al.* [67] for  $Eu$  in  $Yb$  metal and recently in  $LuAl_2:Gd$  by Rettori *et al.* [68].

$Pd$  serves as the best metal for directly observing the long range static conduction electron polarization caused by magnetic impurities. Giovannini *et al.* [13] showed that exchange enhancement of the host conduction electron susceptibility leads to a reduction of the  $RKKY$  oscillations and a very long range static polarization. The long range, and lack of sign reversal, removes Kittel's condition [13] that  $RKKY$  polarization does not give rise to a  $g$  shift but only a line broadening. In fact, additional  $g$  shifts were observed for  $Pd:Gd$  when other rare earth impurities (especially  $Nd$  and  $Tb$ ) were added. This additional shift was proportional to the magnetic susceptibility of the added magnetic impurity, but the sign was negative for rare earths with less than half filled  $4f$  shells, and positive for rare earths with more than half filled  $4f$  shells. This behavior enabled Peter *et al.* [69] to demonstrate that the exchange interaction between the magnetic ions and the conduction electrons was primarily associated with the spin component of the rare earth moment. From the ratio of the additional shift to the additional width, Peter *et al.* were able to show that the range of interaction in  $Pd$  is very large, about ten lattice constants.

Because of the crystalline field (fine structure splittings), the  $EPR$  of  $Gd$  in insulators can be very anisotropic both in cubic (the metal equivalent might be  $Pd$ ), and in hexagonal crystals (the metal equivalent might be  $Mg$ ). The powder resonance spectrum in a metal should therefore depart significantly from a Lorentzian. Nevertheless, a great amount of information about the magnetic impurity-conduction electron exchange interaction, and the magnetic resonance bottleneck has been obtained from powders. Significantly, in most cases the observed line shape was Lorentzian. The reason for this behavior is now understood in terms of exchange narrowing of the fine structure. Recent  $EPR$  experiments in single crystals of  $Mg:Gd$  [44],  $Y:Gd$  [70],  $Au:Gd$  [4], and  $Pd:Gd$  [46] have explicitly exhibited this behavior.

Consider first the case of  $Mg:Gd$ .  $Mg$  is an hexagonal host, and the  $EPR$  in powders has shown that the system is bottlenecked. In single crystals, only a single line was observed (seven should have been seen) with a large axial anisotropy in field for resonance and linewidth at low temperatures. The anisotropy decreases with increasing temperature, and increases with increasing frequency, as shown in Figures 1 and 2 of Reference 44. The analysis of this spectrum is straightforward assuming that: (a) The spin Hamiltonian is  $\mathcal{H} = g\mu_B (\vec{H} \cdot \vec{S}) + D [S_z^2 - (1/3)S(S+1)]$ , and (b) The position of the observed line is at the center of gravity of all the lines



expected from the Hamiltonian (a) for a given angle between the external magnetic field and the  $c$  axis. Then, at high temperatures where the difference in Boltzman factors is small, the spectrum is symmetric and the resonance isotropic at the position given by  $h\nu = g\mu_B H$ . At lower temperatures, or higher magnetic fields, the difference in Boltzman factors increases. The higher Zeeman levels are depopulated, and the center of gravity shifts (anisotropically) as observed. The magnitude of the shift enables one to extract  $D$  using a first moment analysis, even in the absence of resolved spectra. Using this value, the second moment of the fine structure spin-Hamiltonian can be computed immediately. One obtains a result nearly a factor of five larger than the observed linewidth.

Qualitatively, this behavior is understood as follows: For a bottlenecked system, the magnetic impurity and conduction electron spins are tightly coupled. As a result, a phase coherence exists between the two spin species. A spin flip at one site ( $S_z^i \leftrightarrow S_z^i \pm 1$ ) is correlated with a flip in the opposite direction at another site ( $S_z^{i'} \leftrightarrow S_z^{i'} \mp 1$ ). This causes correlated hopping between fine structure lines, and hence a narrowing of the spectrum. In addition to this narrowing mechanism, another always operates for fine structure, independent of whether a bottleneck exists or not. This process is one where the single magnetic impurity flips by virtue of the same exchange process, but only a single site is involved. Transitions between fine structure lines cause a narrowing, but only to the Hebel-Slichter limit (8).  $Mg$  is a case where both processes are operative.

For  $Gd$  at cubic sites, the center of gravity is approximately isotropic except at very low temperatures ( $\lesssim 0.1 K$ ) where only the lowest Zeeman level is populated. Therefore, the collapsed single crystal spectrum should show no anisotropy in  $g$  value (though there should be anisotropy in the linewidth). *EPR* of  $Gd$  in  $Au$  [45] was the first to exhibit partially resolved fine structure in the  $[100]$  direction where the splitting of the spectrum is the greatest. In other directions, a change of linewidth was observed roughly proportional to the expected second moment in the absence of a bottleneck.

$Pd:Gd$  (cubic) exhibits a fully resolved spectrum [46] in the  $[100]$  direction at  $1.4 K$ . The character of the spectrum changes strongly with temperature because of single site line hopping (described above) in the absence of a bottleneck.

These three examples can explain why the *EPR* of  $S$ -state ions can be investigated, even in powders. The averaging and narrowing of the spectrum, very strong for bottlenecked systems but also present to a lesser extent in unbottlenecked systems, reduces the fine structure splitting and results in a narrow Lorentzian powder pattern.

## 2. Non $S$ -state impurities

Single crystals are needed to investigate non  $S$ -state magnetic impurities, except for those cases where a cubic doublet  $\Gamma_6$  or  $\Gamma_7$  lies lowest. Except for recent work by Davidov *et al.* [28] on intermetallic compounds, all resonance work on non

*S*-state impurities has been carried out in elemental hosts. The periodic table of the elements is shown below. The magnetic impurities whose *EPR* has been measured in each host metal is exhibited in diagrammatic form (for references, see Appendix 1). It is seen that, so far, only the resonance of the *S*-state impurities *Gd*, *Eu* and *Mn*, and the four non *S*-state impurities *Ce*, *Dy*, *Er* and *Yb* have been observed. The *EPR* of *Cr* in *Cu* was reported using *TESR* [72]. The diagram shows that though only a few magnetic impurities have been seen, there are a plethora of elemental hosts which have been investigated. The study of the *EPR* in elemental hosts, and the tabulation of the resonance properties in a systematic fashion, can enable one to obtain a better understanding not only of the resonance phenomenon itself, but also of the host metal.

In the following, the results obtained for two rare earths, *Dy* and *Er* (both  $J = 15/2$ ), are given with reference to the properties of the ground level, and of the sign of the crystalline field parameters.

Table 2 gives the assignment of the *Er* ground state for all the 12 coordination cubic elemental hosts measured so far. In most, *Er* possesses a  $\Gamma_7$  ground state. For *Pd*, the ground state is  $\Gamma_8$ , and in *Pt* the ground state is  $\Gamma_6$ . Table 3 gives the same assignments for *Dy*. Here again, the ground state for most hosts is  $\Gamma_7$ , except in *Pd* and *Au* where it is  $\Gamma_8$ , and in *Pt* where one is led to conclude that the  $\Gamma_8$  lies lowest because the resonance has not been observed in powders (single crystals have not yet been attempted). Tables 2 and 3 show that there are two conclusions regarding the relative signs of  $x$  and  $W$ , the parameters defined in terms of the fourth and sixth order crystal field parameters,  $B_4$  and  $B_6$  respectively, by Lea, Leask and Wolf [73]:

$$\begin{aligned} B_4 F(4) &= Wx; \\ B_6 F(6) &= W(1 - |x|). \end{aligned} \tag{13}$$

$F(4)$  and  $F(6)$  are numerical constants. With the exception of *Pt* and *Pd* (see below), these conclusions are:

$$\begin{aligned} &x \text{ is positive (+) and } W \text{ is positive (+);} \\ \text{or } &x \text{ is negative (-) and } W \text{ is positive (+).} \end{aligned} \tag{14}$$

To determine which of the two possibilities is more probable, the systematic variation of  $x$  and  $W$  for *Er* and *Dy* in the four adjacent elements of the periodic table, *Pd*, *Ag*, *Pt* and *Au*, is instructive. In some of these hosts, the ground state for *Er* and *Dy* is  $\Gamma_8$ . Therefore, the sign of  $W$  and the sign and value of  $x$  are determined [74]. Assuming that  $x$  and  $W$  change in a continuous manner for adjacent elements, and using additional information obtained on some  $\Gamma_7$  ground states [75], it is possible to assign the sign of  $x$  and  $W$  for *Dy* and *Er* in the four elements. From the sign of  $x$  and  $W$ , the sign of the fourth and sixth order crystal field coefficient,  $C_4$  and  $C_6$ , are determined. They are given in Table 4, where comparison with that obtained from a point (positive) charge model is made.

Although one does not expect to obtain numerical agreement between the point charge model and the experimental results, it may be expected that at least the sign of the crystal field parameters should agree. The simplest approach in metals would yield a sign corresponding to a positive charge on the neighbouring atoms. However, it has been argued [75] that a partially filled, crystal field split, *d*-like screening orbital may overcome the point charge contribution, resulting in an opposite (or overscreened) sign for  $C_4$ . The sign of  $C_6$  should not be affected as *d* functions do not contribute to  $C_6$ . This agrees with the results for *Ag* and *Au* hosts. For *Pd* and *Pt*, the sign of  $C_4$  is consistent with the above argument, but the sign of  $C_6$  is reversed. This result is not understood, but may arise from the presence of local *f*-like character in the charge density surrounding the rare earth impurity. Regarding *Pd* and *Pt* as exceptions, we obtain a negative sign for  $C_4$  and a positive sign for  $C_6$  for all elemental hosts in Tables 2 and 3.

The analysis of the  $\Gamma_8$  spectrum of *Er* [76] and *Dy* [48] in *Pd* yields additional information. The spectrum of the  $\Gamma_8$  in *Pd:Er* is probably the cleanest ever reported for a non *S*-state impurity. It exhibits a small splitting between the  $-3/2 \leftrightarrow -1/2$  and the  $1/2 \leftrightarrow 3/2$  transitions along *one* of the four equivalent [111] directions (the two resonance fields should be equal for a pure  $\Gamma_8$  spectrum). This splitting was observed only in thin crystals grown by the recrystallization technique. Crystals grown by zone melting did not exhibit this splitting, but instead exhibited a rather broad resonance line without structure at the same angle. This behavior can be understood upon the basis of Zeeman mixing between the excited and ground levels. This was first pointed out by Praddaude [29, and Phys. Letts., to be published], and later exploited by Zingg *et al.* [76a]. Static strains are responsible for the broadening in the zone melting samples [Zevin and Shaltiel, private communication, and to be published].

For *Pd:Dy*, one can only fit the angular dependence of the field for resonance for one of the  $\Gamma_8$  transitions:  $1/2 \leftrightarrow -1/2$ . Yang *et al.* [30] have shown that this difficulty can be removed by the use of a suitable anisotropic exchange Hamiltonian, in conjunction with Praddaude's observation [29] of a close lying excited  $\Gamma_8$ . Anisotropic exchange interactions were also suggested by Kaplan [77] to explain *NMR* results in ferromagnetic metals.

Finally, deviations from the linear temperature dependence of the linewidth as predicted by (8) have recently been observed in a number of dilute alloys [28]. The clearest case was that of *Au:Er* (ground state  $\Gamma_7$ ) at temperatures higher than 6 K. This deviation has been attributed to transitions to the low lying  $\Gamma_8$ . Using Hirst's expression [78] for the *EPR* linewidth caused by inter-level transitions, a limit was obtained on the position of the excited  $\Gamma_8$  level. As *x* was unknown for *Au:Er*, an estimate of the overall crystal field splitting parameter *W* could not be obtained. This could in principle be done if a  $\Gamma_8$  state lay lowest (*x* can be accurately determined), and work on *Au:Dy* to exhibit this effect is in progress [79].



### III. SUMMARY OF THEORETICAL DEVELOPMENTS

The preceding sections have outlined the conceptual history, and the experimental framework, of *EPR* in dilute magnetic alloys. In this section we shall examine in some depth the origin of the various parameters which enter in the analysis of experimental spectra. We begin with a detailed discussion of the magnetic impurity-conduction electron exchange coupling, then go on to the fine structure (interaction between the magnetic moment and its local crystalline environment). We discuss the current theoretical status of the four relaxation parameters which enter the molecular field description of the coupled response function. We conclude with some speculations about future developments in the field.

We do not discuss the validity of the molecular field equations themselves, because curiously enough all the valid microscopic calculations [14] reproduce them with only minor differences, these usually relating to the low temperature form and spin dependence of the relaxation rates.

#### *The Exchange Coupling*

The fundamental differences between insulators and metals, leading to field-for-resonance shifts and resonance line broadening, is the localized-conduction electron exchange interaction. This coupling to the spin or orbital moment of the magnetic ion [31, 33] and its time reversal properties (odd powers of the impurity spin operator) make possible shifts and transition which are forbidden for phonon interactions (even powers of the orbital operators). Thus, the exchange coupling can induce transitions directly between time reversed doublets of half integral spin (so-called Kramers transitions) whereas phonon interactions in the absence of magnetic or exchange fields cannot. In addition, the large magnitude of the exchange interaction (between 0.1 and 1 *eV*), and the strength of conduction electron spin fluctuations, combine to give large values for transition rates. Thus, the fastest lattice relaxation of spin states in insulators known at the low temperature end of the liquid helium range is of order  $10^{-6}$  sec, whereas dilute magnetic alloys routinely possess relaxation times of  $10^{-9}$  sec and shorter. We shall see that this eliminates one candidate for the elusive  $\delta_{iL}$ , the lattice relaxation rate of the magnetic impurity.

The form of the exchange coupling which has been most commonly used in microscopic calculations is,

$$\mathcal{H}_{ex} = (J/N) \sum_i \vec{S}_i \cdot \vec{s}(\vec{r}) \delta(\vec{R}_i - \vec{r}), \quad (15)$$

where  $J$  is the exchange integral,  $N$  is the number of cells per unit volume,  $\vec{S}_i$  the (Russell-Saunders) free ion spin at the position  $\vec{R}_i$ , and  $\vec{s}(\vec{r})$  the conduction electron spin at the position  $\vec{r}$ . The delta function results in a purely local interaction, and allows for only  $s$ -wave scattering. The above form leads to an unbottlenecked  $g$  shift for the localized spin given by (8). Measurement of the shift, and knowledge of  $N(E_F)$ , obtainable from the specific heat density of states corrected for phonon-electron interactions (phonon mass enhancement does not contribute to magnetic properties), enables one to determine both the sign and magnitude of the exchange coupling constant  $J$ . It must be emphasized that two major assumptions have been made in such an analysis: first, isotropy of the exchange coupling; and second, the local character of the exchange coupling. We shall see below that both are in general incorrect. The origin of (15) in metals is a complicated question. First, since the interaction resembles the intra-atomic exchange interaction, a contribution of that nature must certainly be present. As pointed out in Section I, Slater has proven [15] that such a contribution,  $J_{at}$ , will always be positive. It is typically of the order of 0.1 to 0.2  $eV$  for most rare-earths in dilute alloys. Another contribution to  $J$  (inter-atomic exchange) is non-local, and so cannot be written as (15). We shall see below how (15) must be modified to take into account non-locality. Finally, the last important contribution,  $J_{cm}$ , arises from interband mixing (covalency) between the localized magnetic impurity and the conduction electrons. Admixture repels like spin-direction localized and conduction electron states, stabilizing opposite spin-direction conduction electrons, and leading to an effective antiferromagnetic interaction, or a negative sign for  $J_{cm}$ . This interaction is responsible for the negative  $g$  shift of  $Au:Yb$ , and is expected to dominate for most transition metal local moments. Its size varies markedly with the magnitude of the mixing element,  $V_k$ , and the distance of the magnetic level from the Fermi surface ( $E_\uparrow$  and  $E_\downarrow = E_\uparrow + U$ , where  $U$  is the coulomb repulsion on the magnetic ion) [21]:

$$J_{cm} = \frac{V_k^2 U}{E_\uparrow(E_\uparrow + U)} . \quad (16)$$

It has been possible to separate  $J$  into its component parts,  $J_{at}$  and  $J_{cm}$ , for  $Au:Yb$  [41]. For transition metal impurities, recent high temperature nuclear magnetic resonance experiments on the impurity magnetic ion ( $Cu:Mn$ ) by Walstedt and Warren [80] have shown that in the solid state  $J = J_{cm} \cong -1.2 eV$ . Alloul and Bernier [81] have derived a value twice as large at low temperatures as a result of a very careful analysis of the host nuclear magnetic resonance in  $Cu:Mn$ . Götze and Schlottmann [22] presented to this conference their most recent results on the Kondo effect. They appear to be consistent with a temperature variation of this magnitude for the effective exchange coupling as exhibited in the change of magnetization and spin flip rate of the localized moment.

The values for  $J_{at}$  appear to be remarkably constant for rare earths in simple metals. For example, the noble metals exhibit [82]:

Impurity	Host	Exchange derived from linewidth measurements (in eV)
<i>Gd</i>	<i>Ag</i>	0.18
<i>Dy</i>	<i>Ag</i>	0.17
<i>Er</i>	<i>Ag</i>	0.15
<i>Gd</i>	<i>Au</i>	0.2
<i>Dy</i>	<i>Au</i>	0.14
<i>Er</i>	<i>Au</i>	0.1
<i>Yb</i>	<i>Au</i>	(-) 0.3

The modest changes in *Au* are most certainly associated with increasing (negative)  $J_{cm}$  as one moves across the second half of the rare earth series, until *Yb* where  $E_{\downarrow}$  is sufficiently close (from above) to the Fermi energy that  $J_{cm}$  actually overcomes the positive  $J_{at}$ . The latter is associated with the exchange between the  $4f$  and  $5d$  (or better,  $d$ -like) states in the immediate vicinity of the rare earth. Thus, exchange shifts or relaxation should be associated with the exchange interaction between the  $4f$  and  $d$  screening electrons, which then is communicated to the host conduction electrons. Hence, the observed exchange is most certainly not characteristic of the pure or "screened" atomic exchange, but includes matching corrections between the atomic-like  $d$  states and the conduction electrons. The constancy of  $J_{at}$  is therefore all the more remarkable in view of the complexity of the local environment.

It was recognized quite early that the exchange coupling was most definitely not isotropic, as implied by (15). In general, the exchange should be written as:

$$\mathcal{H}_{ex} = (1/2 N) \sum_i \sum_{\alpha\beta} J_{\alpha\beta} \left[ \frac{1}{2} + 2 \vec{s}_{\alpha}(\vec{R}_i) \cdot \vec{s}_{\beta}(\vec{r}) \right] \delta(\vec{R}_i - \vec{r}) \quad (17)$$

where  $\vec{s}_{\alpha}(\vec{R}_i)$  is the spin of the  $\alpha$ th electron at the local moment site  $\vec{R}_i$ , and  $\vec{s}_{\beta}(\vec{r})$  the  $\beta$ th electronic state in the conduction band at  $\vec{r}$ . For conduction electrons of other than  $s$  character at the local moment site, the  $J_{\alpha\beta}$  are most certainly not all equal. If they were, the  $J_{\alpha\beta}$  could be removed from the sum, and the sums over  $\alpha$  and  $\beta$  carried out immediately to yield the original form (15). For an  $S$ -state ion, one can write  $\vec{s}(\vec{R}_i) = \vec{S}_i/n$ , where  $n$  is the number of localized electrons, and again the spin dependent part of the interaction could be written in isotropic form [83]

$$\mathcal{H}_{ex} = (1/N) \left[ \sum_{\alpha\beta} (J_{\alpha\beta}/n) \right] \sum_i \vec{S}_i \cdot \vec{s}_{\beta}(\vec{r}) \delta(\vec{R}_i - \vec{r}). \quad (18)$$

For multiple bands, Jaccarino and Yafet [83a] have shown that the various orthogonal components  $\beta$  of the conduction electron states do not interfere, and the  $g$  shift and

linewidth calculated from each band (e.g.  $s$  and  $d$  in the transition metals) add. Under these conditions, (18) reduces effectively to (15).

If neither of these conditions (all  $J_{ij}$  equal, or an  $S$ -state ion) are fulfilled, then the exchange interaction cannot be written in isotropic form. As Van Vleck and Huang [84], Koide and Peter [31], as well as Coqblin and Schrieffer [32] have shown, (dropping the  $j$  subscript for the conduction electrons because of the additivity mentioned above) one can write for cubic symmetry (omitting conduction electron orbital terms):

$$\mathcal{H}_{ex} = \left[ \frac{1}{N} \right] \sum_i [A_0 + A_4 O_4(L_i) + A_6 O_6(L_i)] [\vec{S}_i \cdot \vec{s}(\vec{r})] \delta(\vec{R}_i - \vec{r}), \quad (19)$$

where  $A_0$  is the isotropic exchange constant of (15), and  $A_4, A_6$  are the anisotropic exchange coefficients. The last,  $A_6$ , does not contribute for  $d$  electrons. The operators  $O_4$  and  $O_6$  are the standard operator equivalents [85], their argument being the orbital operator for the local moment ground Russell-Saunders state. This is the most general form for the exchange coupling in a cubic environment (on the assumption that the conduction electron orbital moment is quenched). The generalization to other point group symmetries is obvious. In concentrated systems (e.g. the rare earth metals) the above expression together with the Ruderman-Kittel interaction will yield a very anisotropic exchange coupling for propagating spin wave states. In dilute alloys, the effect of the anisotropy will be subtle. For example, in rare earths with crystal field split spin doublets for ground states, the anisotropy generated by (19) will not be seen (an  $S = \frac{1}{2}$  state cannot exhibit cubic anisotropy). As a result, the exchange will be isotropic, with, however, contributions from the projection of the 0th, 4th and 6th order terms from (19) onto the ground spin-Hamiltonian.

The anisotropy will appear in a  $\Gamma_8$  manifold. In such a case, Bleaney [74] has shown that the field for resonance can be represented by using a fictitious spin  $S = 3/2$ :

$$\mathcal{H} = \sum_i [g\mu_B \vec{H} \cdot \vec{S}_i + f\mu_B \{H_x (S_i^x)^3 + H_y (S_i^y)^3 + H_z (S_i^z)^3\}], \quad (20)$$

where the superscripts stand for the cartesian components of the spin. The coefficients  $g$  and  $f$  are determined by the crystalline field, being unique for non-repeating  $\Gamma_8$  states (e.g.  $Ce$ ,  $Sm$  and  $Yb$ ). For repeated  $\Gamma_8$  representations,  $g$  and  $f$  depend on the fourth to sixth order crystalline field coefficient ratio. This is the case in the absence of anisotropic exchange. If one admits this anisotropy by inclusion of (19), then the uniqueness of fit for an isolated  $\Gamma_8$  multiplet is removed. The  $g$  shift caused by the anisotropic exchange will project into the same form as (20) but contributions to  $g$  and  $f$  will be different for each of the three coefficients in (19). Hence, the ratio of  $f$  to  $g$  will no longer uniquely determine the crystalline field ratio, but rather will involve that ratio and the three anisotropic exchange parameters. Devine *et al.* [48] have shown that the parameter representative of the crystalline

field ratio,  $x$ , equals  $+0.465$  for  $Pd:Er$ , while they were unable to assign a value for  $x$  for  $Pd:Dy$ . Using magnetic susceptibility measurements at very high fields, Praddaude [29] has arrived at essentially the same value for  $x$  for  $Pd:Er$ , but  $x = -0.5418$  from a fit to the *EPR* results of Reference 48, and  $x = +0.75$  from susceptibility measurements. If the crystal field changes only slightly going from  $Er$  to  $Dy$  in  $Pd$ , these values of  $x$  cannot be correct. In particular, if  $x$  is positive for  $Er$ , it must be negative for  $Dy$ . The discrepancies can no doubt be ascribed to the absence of anisotropic exchange in their analysis, and the fact that the  $g$  shifts due to exchange are very large for rare earths in a  $Pd$  host. It turns out that for  $Pd:Dy$ , Praddaude has shown that two  $\Gamma_8$  double the ground manifold to eight states. As a result, by fitting to the measured fields for resonance, Yang *et al.* [30] have obtained all the anisotropic exchange parameters, as well as the crystalline field parameters. A useful check can be made on their determination of  $A_0$ , for it represents the simple sum of all the one electron exchange integrals, and so should nearly equal  $J$  determined from  $S$ -state ion ( $Gd$ ) measurements. The value found for  $Pd:Dy$  agrees with  $GdJ(\vec{q}=0)$  ( $g$  shift) found by Devine *et al.* [46].

Finally, other forms of exchange, acting between the orbital moment of the conduction electrons and the impurity orbit, or between the spin (orbit) of the conduction electrons and the orbital (spin) moment of the impurity, are most certainly present. The former has been investigated by Kondo [17], Giovannini [33], Hirst [33] and Yafet [8]. It leads to a lattice relaxation rate of the localized spin ( $\delta_{iL}$ ) proportional to  $T$ , and to a large skew scattering leading to an extraordinary Hall effect in dilute rare earth magnetic alloys. The latter contributes to the spin flip scattering cross section of conduction electrons. Giovannini [33] and Hirst [33], independently, have tabulated all of the various group theory allowed forms for the interaction between the local moment-conduction electron spins and orbits.

Besides the shift in the field for resonance, and transport measurements, the anisotropic exchange Hamiltonian (19) can also cause spin flip relaxation where the local moment changes its Zeeman state by more than a single unit. For  $d$  electrons,  $M_J$  can change by as much as 5, and for  $f$  electrons by as much as 7. This was first explicitly noted by Coqblin and Schrieffer [32].

In addition to the exchange interaction, the local moment also experiences a crystalline field characterized by the local site symmetry. Splittings of the order of  $100\text{ cm}^{-1}$  ( $0.01\text{ eV}$ ) for rare earths, and of order  $1\text{ eV}$  for iron group impurities, are typical. The rare earth splittings appear to be about a factor of two to three smaller than in insulators. Only primitive information is available for transition metal impurities in metals, but a similar reduction is expected, especially in view of the energy overlap of the virtual  $d$  bound states. The origin of the crystalline field still remains a mystery. The most successful model which appears to account for the crystalline field splitting in the noble metals is that originally proposed by Coles and Orbach, and first made quantitative by Williams and Hirst [75], and later



Chow [86]. In their model, the rare earth is surrounded by  $d$ -like screening electrons. A simple pseudopotential argument would suggest a  $5d$ -like orbital for rare earths in mono- and di-valent hosts. In such cases, the  $d$  state is split by the host crystal field. The width of the  $d$  state is too great for a moment to appear, but if the splitting exceeds the width, the symmetry of the local screening charge is reduced from spherical to cubic. The intra-atomic coulomb and exchange interactions then transmit to the  $4f$  electrons this reduction of symmetry, and a cubic splitting of the  $4f$ 's occurs. The entire process is the reverse of the crystal field screening process envisaged by Watson and Freeman [87], and as a result always acts opposite to the potential acting on the  $d$  electrons. Screening  $d$  electrons contribute only to the fourth order crystalline field term. As Davidov *et al.* [28c] have recently shown, evidence exists for  $f$ -like screening, leading to substantial contributions to the sixth order crystalline field term.

The case of the  $d$  local moments is another matter. In most cases, the  $d$  level width exceeds the crystalline field splitting so that no cubic character is exhibited by the local moment resonance. Indeed, no fine structure has yet been reported for transition metal local moment resonances. It has been carefully searched for in  $Cn:Mu$  [88] and  $Ag:Mn$  [89]. The overlap in energy of the broadened  $d$  orbital states has been argued [47] as the reason for the reversal of the ground and first excited state ordering in  $Au:Dy$  and  $Ag:Dy$  (the  $d$  levels are broader in the latter leading to a smaller fourth order crystalline field). The smallness of the cubic fine structure parameter even in insulators (being proportional to the fourth order perturbation of the spin orbit coupling) may combine with this reduction to make fine structure unobservable in cubic hosts. In hexagonal hosts, however, the fine structure is only second order in spin orbit coupling, and therefore much larger in insulators than cubic terms. Hence, examination of hexagonal hosts doped with  $Mn$  may yield evidence of crystal field splittings, hopefully even resolved.

Resolved fine structure was reported at the Conference by B. Elschner [90] for  $BaAl_4:Eu$  (hexagonal) and Moret *et al.* [91] for  $Pd:Gd$  (cubic). An extensive analysis of the latter showed that two superposed resonances were observed: one was that due to the cubic field splitting of the  $Gd$  ( $S = 7/2$ ) resonance line, while the other was at the  $\pm \frac{1}{2}$  transition frequency of the  $Gd$  line. The latter diminished in intensity as the concentration of  $Gd$  was lowered. However, it was clearly visible even in a 300 *ppm* sample. Curiously enough, its position in a 1,300 *ppm* sample was not at  $g = 1.78$ , appropriate to that concentration, but rather at  $g = 1.813$ , found by Cottet and Peter [62] for  $Pd:Gd$  (powder) concentrations of 8,000 *ppm*. This indicates non-uniformity of the  $Gd$  solute. R. H. Taylor and B. R. Coles pointed out ([92], and see the discussion) that the residual linewidth in powders broadened with increasing microwave frequency. Davidov [93] commented that this was due to a distribution of  $g$  values associated again with non-uniformity of the  $Gd$  concentration (also see the discussion).

Observation of fine structure and its magnitude, are related to the fundamental question of the character of the magnetic state in the metal. The rather well-behaved rare earths exhibit splittings representative of a well localized magnetic state. Hartree-Fock local moment theory is clearly inapplicable, and one resorts immediately to a Russell-Saunders ionic model for the magnetization. Hirst [35] has proposed a similar approach for the transition metals. He first uses the coulomb potential  $U$  to argue for localization. He then turns on the mixing with the conduction electrons to generate the exchange coupling, then the intra-atomic exchange to produce a Hund's rule ground multiplet. The crystal field then splits these levels, with the spin-orbit coupling finally being invoked. This "ionic" model for the transition metal series (Hirst argues for a divalent configuration in  $Cu$ ) may be a closer approximation to the truth than the naïve Hartree-Fock description. The reason is connected with the strong intra-atomic coulomb correlations once magnetization is achieved. *NMR* measurements on  $Co$  in  $Au$  (the analogue of  $V$  in  $Cu$ ) reported by Narath [94] appear to be consistent with Hirst's divalent ionic assumption. The trouble with the ionic model is that it neglects the effects of  $d$ -level breadth and its influence on the Russell-Saunders coupling as well as the crystalline field splitting (this breadth is in the Hartree-Fock occupation number sense and is not associated with the directional motion of the moment). At present, finite temperature Hartree-Fock theory is not developed to the point where meaningful calculations can be made of local moment dynamics. Observations of ions other than  $Mn$ , together with fine structure measurements, may well provide intuitive help in the attempt to characterize transition metal ions in metallic hosts.

We have so far discussed the static properties of magnetic resonance in metals. We now turn to the dynamic quantities. Specifically, we examine the four relaxation rates appearing in the molecular field expressions for the coupled localized-conduction electron response functions. They are, in order of increasing complexity,  $\delta_{ie}$ ,  $\delta_{ei}$ ,  $\delta_{eL}$  and  $\delta_{iL}$ . We treat each of them separately.

$\delta_{ie}$ :

The localized-to-conduction electron relaxation rate was first calculated for the analogous case of nuclei by Heitler and Teller [95]. The connection with the square of the Knight shift was made by Korringa [96]. For isotropic exchange of delta function range dependence,

$$\delta_{ie} = \pi [JN(E_F)]^2 kT/\hbar \quad (21)$$

at temperatures  $\frac{kT}{\hbar} \gg \omega$ , or  $\omega_0$ , the measuring or Zeeman frequency respectively.

(The difference between (8) and (21) lies with the units. (8) refers to linewidth in  $G$ , and (21) to the linewidth in frequency units. Thus (8) equals (21) divided by

$\frac{g\mu_B}{\hbar} = \frac{2\mu_B}{\hbar}$  for true spin states.) If exchange enhancement exists between the conduction electron spins, the above is multiplied by  $\frac{K(\alpha)}{(1-\alpha)^2}$ , and the relationship between the  $g$  shift and the linewidth parameter  $\delta_{ie}$  becomes [96]

$$kT(\Delta g)^2 / \hbar \delta_{ie} = \frac{1}{\pi K(\alpha)}. \quad (22)$$

For many materials the relationship (22) is violated and the discrepancy cannot be blamed on exchange enhancement (e.g. *Pd:Gd* [46] where there is still an order-of-magnitude discrepancy after using the Doclo *et al.* [97] value for  $\alpha$ ). The reason for the discrepancy has been argued to be the assumption of a delta function range for the exchange [24]. If one relaxes this condition, the exchange constant can be written (note that we must assume a spherical Fermi surface even for this form):

$$J(\vec{k}, \vec{k}') = J(\vec{q}) = \sum_L (2L+1) P_L(\cos \varphi) J^{(L)}(k_F, k_F) \quad (23)$$

where  $\vec{q} = \vec{k} - \vec{k}'$  and  $|\vec{q}| = 2k_F(1 - \cos \theta)^{1/2}$ . With this form, noting that the  $g$  shift is proportional to the  $\vec{q} = 0$  component of the exchange (since the measuring rf wavelength is large compared to the sample size), the  $J$  in (7) should be replaced by

$$J(0) = J^{(0)} + 3J^{(1)} + 5J^{(2)} + 7J^{(3)} + \dots \quad (24)$$

For the linewidth, what is important is the square of  $J(\vec{q})$ , summed over all wave vectors from 0 to  $2k_F$ . The effective square of the exchange which should replace  $J^2$  in the expression for  $\delta H_0$ , (8), and for  $\delta_{ie}$ , (21), is

$$\langle J^2(\vec{q}) \rangle = (J^{(0)})^2 + 3(J^{(1)})^2 + 5(J^{(2)})^2 + 7(J^{(3)})^2 + \dots \quad (25)$$

At first sight, (24) and (25) would alter the Korringa relationship (22). In fact, (25) is only valid in this context if there is no exchange enhancement. Thus, in the absence of exchange enhancement, one can modify the Korringa relation by the use of (24) and (25) in their respective positions. In the presence of exchange enhancement, (24) remains the same, but (25) becomes:

$$\begin{aligned} \langle J^2(q) \rangle &= \sum_{L, L'} (2L+1)(2L'+1) J^{(L)} J^{(L')} \\ &\times \left\langle \frac{P_L(\cos \theta) P_{L'}(\cos \theta)}{[1 - U \chi(\cos \theta)]^2} \right\rangle \end{aligned} \quad (25')$$

where  $U \chi(1) = \alpha$ ,  $\chi(\cos \theta)$  being the real part of the  $q$  dependent susceptibility.

It is seen from (25') that cross terms are present between the  $J^{(L)}$  which would otherwise vanish if  $\alpha = 0$  (i.e. no exchange enhancement of the conduction electron



gas). This complicates any analysis, but must be taken into account when simultaneously one has present wave vector dependent exchange and exchange enhancement. This important contribution was first calculated by R. E. Walstedt and L. R. Walker (to be published). The various partial wave amplitudes  $J^{(L)}$  also contribute to the electrical resistivity and Kondo resistivity, but in a more complicated manner. The full expressions for the transport properties including potential scattering effects can be found in the paper of Fisher [98].

Though it may seem as though (23) does not provide much simplification, in fact the series converges rather well as  $L$  increases. The main features are the following. Each partial wave has a (positive) contribution from the atomic exchange which Watson [99] has shown falls off rapidly with increasing  $L$  (though this may be in dispute by virtue of very recent skew scattering experiments of Friederich *et al.* [100]). The (negative) contribution to  $J^{(L)}$  from inter-band mixing is maximal for  $L = l$ , the orbital angular momentum of the electron in question. Because of the nearly spherical symmetry of the mixing potential (and the certain inversion symmetry) the only other significant mixing contributions can occur in the  $L = l \pm 2$  channels. Thus, for  $d$  electrons, one should sensibly terminate (23) after  $L = 2$ , and for  $f$  electrons after  $L = 3$ . The two quantities measured in magnetic resonance,  $\Delta g$  and  $\delta_{ie}$ , give two equations for the  $L$  wave coefficients. The electrical resistivity and Kondo resistivity give two more, so that all the significant partial wave amplitudes can be determined, in principle. It appears possible that  $Au:Yb$  can be so analyzed by virtue of the *EPR* results of Tao *et al.* [41], the electrical resistivity measurements of Murani [101], and the Mössbauer measurements of Gonzales and Imbert [102] (see below).

Walker [103] has carried out the calculation of  $\delta_{ie}$  to third order in  $J$  and obtained the Kondo terms:

$$\hbar\delta_{ie} = \pi [JN(E_F)]^2 kT \left[ 1 + 2JN(E_F) \ln \frac{kT}{D} \right] \quad (26)$$

where  $D$  is the effective conduction electron bandwidth. For effective spin states one should replace  $J$  by  $g [(g_J - 1)/g_J] J$ . The logarithmic term has been reported by Gonzales and Imbert [102]. It is interesting to note that the large residual width apparently inherent in all *EPR* experiments makes it nearly impossible to obtain an accurate temperature dependence for  $\delta_{ie}$ . However, the Mössbauer effect is insensitive to static broadenings, and only responds to dynamic spin flips. For this reason, the inherent accuracy of the Mössbauer analysis is much greater in the intermediate region between fully resolved and fully narrowed spectra. If this happens to occur when the temperature is in the convenient helium range, (as it does for  $Au:Yb$ ) an accurate measure for  $\delta_{ie}$ , including Walker's [103] third order terms, can be obtained [104]. It is important to note that the Mössbauer measurements [102] for  $\delta_{ie}$  fall within the error limits of the *EPR* measurements [41].

At low temperatures, Orbach and Spencer [105] have derived an expression for  $\delta_{ie}$  (their expression applies more generally to non-cubic materials but we have reduced it to the cubic case for convenience here. See also Walker [103]):

$$\hbar\delta_{ie} = \frac{\pi}{2} [JN(E_F)]^2 \{k_B T + \frac{1}{2} \hbar\omega_0 \coth \left[ \frac{\hbar\omega_0}{2k_B T} \right] \} \quad (27)$$

Their expression holds only for spin  $\frac{1}{2}$  by virtue of one of their decoupling approximations. It was generalized to arbitrary spin by Götze and Wölfle [106]:

$$\begin{aligned} \hbar\delta_{ie} = & \left( \frac{\pi}{4} \right) [g_i \mu_B JN(E_F)]^2 \left[ \frac{2B^{eff}}{g_i \mu_B \langle S^z \rangle} \right] \\ & \times \{ S(S+1) - \langle S^z \rangle \left[ \coth \left( \frac{\hbar\omega_0}{2kT} \right) - \frac{kT}{\hbar\omega_0} \right] \} \end{aligned} \quad (28)$$

where  $B^{eff}$  is the effective magnetic field acting on the local moment. It is interesting to separate out two contributions to  $\delta_{ie}$ . The first [last] terms on the right of (27) [(28)] is a result of longitudinal fluctuations of the conduction electron spin (the so-called frequency modulation effect) and goes smoothly to zero as the temperature goes to zero. It is basically a zero frequency effect. The other contribution to  $\delta_{ie}$  is from transverse conduction electron fluctuations, and is equal to one half of  $1/T_1$ , the relaxation rate of the  $z$  component of the magnetization. The latter can be calculated by the golden rule, the former is obtained to equal accuracy in the line-width calculations (27) and (28). In conventional magnetic resonance terminology, the linewidth

$$\delta_{ie} = 1/T_2 = 1/T_2' + 1/T_1' \quad (29)$$

The first [last] term in (27) [(28)] is  $1/T_2'$ , while the other is  $1/T_1' = 1/2T_1$ . At high temperatures  $\frac{1}{T_2'} = \frac{1}{T_1'}$  so that  $\delta_{ie} = 1/T_1$ . We shall see some interesting consequences of the separation between  $1/T_1'$  and  $1/T_2'$  when we discuss  $\delta_{ei}$  below. The net result of these expressions is that for spin  $\frac{1}{2}$  at low temperatures, at  $X$  band, the linewidth does not go to zero, but saturates at half the value which one would have found if one extrapolated his measurements to  $\sim 0.25$  K. This is unfortunate, for it means that most probably the hyperfine spectrum of  $Mn$  in  $Cu$  or  $Ag$  will never be seen as  $\delta_{ie}$  can never be made small enough [80, 81] by going to low temperatures. Low frequencies are also needed, and then sensitivity problems result (see Section II).

The narrowing of hyperfine structure is closely allied to the second (but not the first) process for fine structure narrowing (Section II, or Ref. 27). The phase coherence between the conduction electron and the localized moment spin leads to an effective spatial transfer of magnetization which can result in a narrowing of the hyperfine interaction [38]. The crucial condition is that  $\delta_{ie}$  be greater than the hyperfine splitting.

If the opposite be true, then even in the bottleneck regime the hyperfine splitting can be observed. It now appears that, for *Mn* in *Cu* [80, 81], the exchange is sufficiently large that this condition ( $\delta_{ie}\hbar$  less than the hyperfine splitting) can never be realized in practice. Hence, at present, it appears that the hyperfine splitting of transition metal ions in metals is nearly impossible to observe, and only under the most favorable of circumstances will one be successful. The situation is even worse for fine structure, in that narrowing can occur even in the absence of a bottleneck condition. The difference lies in the fact that single site electron spin flips do not affect the hyperfine spectrum, but alter significantly the fine structure spectrum.

Measurements of  $\delta_{ie}$  have recently been carried to higher temperatures [28a, b]. The temperature dependence was observed to depart from linear, implying direct electron induced transitions between the ground and excited crystal field levels. The activation behavior of the linewidth enables one to extract the splittings between the ground and excited levels. These splittings have been used, in the case of *Au:Er*, to verify the splittings determined by susceptibility measurements [75], and for *Ag:Dy* to correct the susceptibility results [75] which claimed near degeneracy of the ground  $\Gamma_7$  and excited  $\Gamma_8$  levels. With more accurate measurements in the future, this method may prove a useful tool for determining crystal field splittings. In combination with, for example, a  $\Gamma_8$  resonance, enough information could be obtained to yield both the fourth and sixth order crystal field coefficients (apart from the effects of anisotropic exchange). The calculations can also be used for a determination of the Mössbauer line narrowing rate at higher temperatures. Indeed, the Mössbauer [108] and *EPR* temperature dependences for  $\delta_{ie}$  appear in reasonable agreement.

$\delta_{ei}$ :

The conduction-to-localized-electron relaxation rate was first calculated for nuclei by Overhauser [109]. It was adapted to the electron spin case by Hasegawa [3], and turns out to be the controlling factor for the magnetic resonance bottleneck at usual concentrations and temperatures. It is a curious quantity, for no satisfactory low temperature expression exists. The trouble lies in the inability to separate the conduction electron spin propagator from the higher order Greens functions which result as a consequence of the equations of motion. The high temperature expression for  $\delta_{ei}$  is:

$$\hbar\delta_{ei} = (2\pi/3) cN(E_F) J^2 S(S+1) \quad (30)$$

where  $c$  is the magnetic impurity concentration. In the presence of exchange enhancement,  $\delta_{ei}$  is given by (30) multiplied by  $K(\alpha)/(1-\alpha)$ . As shown by Zitkova-Wilcox [59], this leads to satisfaction of the detailed balance condition even in the presence of exchange enhancement

$$\delta_{ie} \frac{\chi_i}{g_i^2} = \delta_{ei} \frac{\chi_e}{g_e^2} \quad (31)$$

$\hbar\delta_{ei}$  equals the conduction electron spin linewidth  $\hbar/T_1$  at high temperatures. If one separates  $\delta_{ei}$  into its component parts, as done for  $\delta_{ie}$ , a curious fact emerges. Calculating the imaginary part of the one electron self energy in the dilute magnetic alloy from transverse fluctuations leads to a spin flip rate equal to  $1/2T_1$ , as with  $\delta_{ie}$ . However, the longitudinal contribution to the imaginary part of the self energy turns out to be half of the transverse contribution, or  $1/4T_1$ , so that the sum  $1/T_2 + 1/T_1 = 3/4T_1$ , a most peculiar result. The interesting resolution of this discrepancy lies with the two electron character of the conduction electron response function. A vertex correction yields only a longitudinal contribution, and results in an additional contribution to the linewidth of  $1/4T_1$ , so that mercifully  $\delta_{ei} \equiv 1/T_2 = 1/T_1$ . This addition of self energy and vertex correction should be compared with potential scattering where, in the  $\vec{q} = 0$  limit, the two exactly cancel. It is only because of the reversal of sign of the longitudinal exchange coupling at the electron and hole vertices that an addition takes place in the case of magnetic resonance. It also represents a warning-calculating one electron properties may be insufficient. Isotropy requires that the full response function be calculated including vertex terms [107].

The quantity  $\delta_{ei}$  controls the bottleneck reduction of  $g$  shift and linewidth. Because the low temperature behavior of  $\delta_{ei}$  is not known, it would be of great interest to work in a bottlenecked system at temperatures low compared to the Zeeman splitting. One would expect a reduction in  $\delta_{ei}$  coming from a depopulation of the various  $S_z$  states, so that the bottleneck could in principal be broken. If the breaking was only partial, an increase in  $g$  shift and linewidth slope should nevertheless be seen, and a hint of the analytic form for  $\delta_{ei}$  obtained.

Another interesting feature is the possibility of conduction electron induced transitions between local moment crystal field states, as for  $\delta_{ie}$ . The conduction electron spin can be flipped by virtue of transitions between the ground crystal field manifold and the first (or higher) excited crystal field levels. Preliminary experiments by Silsbee *et al.* [110] using transmission techniques have found evidence for the transition between the ground  $\Gamma_1$  (non magnetic) and the excited  $\Gamma_4$  level of  $Ag:Tm$ . Conventional reflection *EPR* could never detect the  $Tm$  resonance because of the singlet ground state.

Probably the most useful aspect of the knowledge of  $\delta_{ei}$  lies in the connection with superconductivity. The pair breaking parameter of the Abrikosov-Gorkov theory is just  $\delta_{ei}$ , though without the  $(1 - \alpha)$  diminution factor caused by conduction electron exchange. The depression of  $T_c$  can be predicted from the knowledge of  $\delta_{ei}$ . The relationship is remarkably simple [64, 111]:

$$dT_c/dc = (3\hbar\pi/16k_B)(d\delta_{ei}/dc) \quad (32)$$

If there is no bottleneck so that  $\delta_{ei}$  cannot be obtained directly, detailed balance (31) can be used and  $\delta_{ei}$  predicted from knowledge of  $\delta_{ie}$ , directly measurable in the

absence of a bottleneck. The expression (32) has also been used in reverse [64]. The case of  $LaAl_2:Gd, Ce$  was one where a bottleneck was present, and some estimate of the exchange spin flip rate of the conduction electrons due to the  $Ce$  impurities was desired. Maple's measurements [112] of  $dT_c/dc$  were used to find  $\delta_{ei}$  for  $Ce$  and  $Gd$ . The value for  $Gd$  exceeded that for  $Ce$  by a factor of  $\sim 1.5$ . The  $\delta_{eL}$  was measured for both using  $EPR$  and the bottleneck theory.  $Ce$  exceeded  $Gd$  by a factor of  $\sim 7$ . Because the  $g$  value of  $Ce$  differs significantly from 2, the  $\delta_{eL}(Ce) = \delta_{ei}(Ce) + \delta_{eL}$  (spin-orbit coupling). The only way to reconcile these two results is to argue that the spin-orbit interactions on the  $Ce$  sites dominate the exchange. This prevents a direct measurement of the Kondo temperature dependence for the exchange conduction electron spin flip rate. It also demonstrates that at least down to 1.4 K there is no evidence for a large Kondo enhancement of  $\delta_{ei}$ .

$\delta_{eL}$ :

The conduction electron-lattice relaxation rate is the most easily altered rate of all those which influence the bottleneck conditions. Addition of non-magnetic impurities contributes to this rate (as will indeed even the magnetic species themselves) through spin-orbit scattering [6, 7, 8, 64]. A magnetic impurity can also contribute to this rate via  $\delta_{ei}$ , provided that the added magnetic species is itself not bottlenecked. Should this be the case, a double bottleneck occurs [113] and one can obtain resonance properties from a spin species whose magnetic resonance in reflection cannot be directly observed.

The first satisfactory theory for the rate  $\delta_{eL}$  was given by Yafet [8], and applied to impurities in the alkali metals by Asik, Ball and Slichter [114]. Basically, the conduction electron mixes with the (primarily  $p$ ) states of the impurity. This admixture means that the conduction electron experiences a non-periodic potential which, by virtue of impurity-host contrast in spin-orbit coupling, can result in a spin flip. The rate of flip is governed by the amount of admixture, the magnitude of the spin-orbit contrast, and the virtual localized density of states for the non-magnetic level. Asik, Ball and Slichter found  $p$ -wave scattering to be dominant, even with  $d$  states present on the impurity. Yafet extended his earlier work to magnetic impurities, and presented at the Conference a rather complete picture for the lattice relaxation process. He includes additional terms in the Anderson Hamiltonian which generate the time reversal symmetry necessary for the calculation of magnetic relaxation. For the case of the  $l$ th orbital of non-magnetic impurities, Yafet found [8]

$$\hbar\delta_{eL} = \frac{8\pi c E_F}{9} \sum_l l(l+1)(2l+1) \lambda_{eff}(l)^2 \rho_l^2(E_F) \quad (33)$$

where  $\lambda_{eff} = \frac{\lambda}{[1 + UN(E_F)]}$  and  $\rho_l(E_F) = \frac{\Delta/\pi}{(E_l - E_F)^2 + \Delta^2}$ ,  $\lambda$  and  $U$  being the non-



magnetic impurity spin orbit coupling and coulomb repulsion, and  $\Delta$  the width of the  $l$ th virtual bound state. The quantity  $\delta_{eL}$  can be measured directly from the bottleneck equations [6, 7]. It led to an interesting study in  $LaAl_2$  [64] metal. The presence of two bands behaving rather independently with respect to the bottleneck was exhibited. The addition of impurities broke the bottleneck in the  $s$  band (the  $d$  band was not bottlenecked). In  $Al$ , values for the spin flip rate  $\delta_{eL}$  were obtained [114a] which have since been calculated precisely [114b]. The information from these measurements, taken together with resistivity and superconductivity measurements, provide sufficient information to yield all the parameters which describe the virtual bound state and its enhancement factors.

An interesting check on the spin orbit scattering rate can be obtained from *EPR* measurements in the superconducting state. The  $g$  shift is reduced in the superconductor by an amount proportional to the spin orbit scattering time. Thus, the host susceptibility in the dirty limit, and when  $\hbar\delta_{eL}$  exceeds  $kT_c$ , is given by [115]

$$\frac{\chi^n - \chi^s(0)}{\chi_n} = 2v_F \tau_{s.o.}/\pi\zeta_0 \quad (34)$$

where the superscripts  $n$  and  $s$  indicate normal and superconducting respectively;  $v_F$  is the Fermi velocity;  $\tau_{s.o.}$  is the spin orbit relaxation time (equaling  $1/\delta_{eL}$ ), and  $\zeta_0$  is the coherence length. The reduction of the  $g$  shift of  $Gd$  in  $LaRu_2$  was measured in the superconducting state, and  $\tau_{s.o.}$  was found to equal  $\sim 10^{-14}$  sec. Examining  $\delta_{ie}$  (directly measured), and using detailed balance, it was found that no bottleneck should be present. That is,  $\delta_{ei}$  was much smaller than  $\delta_{eL}$ . An additional check was obtained as the  $Gd$  concentration was increased, the upper critical field exhibited re-entrant behavior ( $H_{c2}$  initially increased as the temperature was lowered, then decreased at lower temperatures). This is caused by a polarization of the  $Gd$  ions, yielding an exchange field and thereby inducing an additional Pauli pair-breaking term in the expression for  $T_c$  and the upper critical field. The effect of this polarization depends on the magnitude of the  $\vec{q} = 0$  value of the exchange field (obtained from the  $g$  shift) and the time for conduction electron (spin-orbit) spin flip. Thus, by measuring the re-entrant curve, the spin-orbit spin flip time could be extracted. It was found to agree crudely with that obtained from the  $g$  shift. This kind of experiment illustrates the powerful connection between *EPR* and superconductivity [111]. The parameters which govern the one are reflected in the other, and the two measurements provide complimentary information concerning the dynamics of conduction and localized electron spins. To amplify this point, Maki [129] showed the exchange conduction electron spin-flip rate,  $\delta_{ei}$ , depends on the temperature below  $T_c$ , increasing as  $T$  is lowered. The spin-orbit conduction electron spin flip rate, however, diminishes as the temperature is lowered. This implies that a bottleneck could develop in the superconducting state even if none existed in the normal state. It would then allow

for the extraction of the *local* conduction electron dynamics in the superconducting state.

An additional theoretical puzzle is present in the magnetic resonance of superconductors. The presence of an electron spin is a powerful pair breaker. The order parameter in the immediate environment of the impurity spin is altered from the bulk or average value. This alteration must affect the local excitation spectrum of the superconductor, and hence the  $g$  shift and line width of the resonance. Such terms have yet to be calculated, but are clearly central to a full understanding of the magnetic resonance problem in the superconducting state.

Finally, at high temperatures the phonon relaxation of the conduction electron spins becomes important. This rate goes as  $T^5$ , and thus exhibits a clear signature [116].

$\delta_{iL}$ :

This mysterious rate has yet to be experimentally observed (in the authors' opinion). The direct relaxation rate of the localized moment spin to the lattice can, of course, occur by phonon induced transition, as in insulators. However, the magnitude of such interactions at low temperatures is much smaller than typical exchange interactions, and direct evidence of phonon effects has yet to be exhibited. Most experiments which have reported values for  $\delta_{iL}$  have measured only residual widths in either *EPR* transmission studies (Schultz *et al.* [55]) or in reflection (Gossard *et al.* [6, 7]). They have assigned a significance to these widths [9] by referring to them as a lattice relaxation rate. It is by no means obvious that this procedure is valid. The widths are most likely nothing more than inhomogeneous broadening, or perhaps even unresolved hyperfine [117] or fine structure. Indeed, even the concentration dependence appears to be peculiar. Shanabarger [118] found an inverse  $Mn\ c^2$  behavior for  $\delta_{iL}$  for *Ag:Mn* at very low *Mn* concentrations, then inverse behavior at higher concentrations. However, Gossard *et al.* [6] found a proportionality to the *Si* concentration for *Cu:Mn*. In our opinion, the results are consistent with exchange narrowed hyperfine structure as the source of the residual width in these two alloys [119]. As stated previously [10], the McElroy-Heeger mechanism [9] for  $\delta_{iL}$  is incorrect.

A number of authors have considered lattice relaxation rates for the localized moments, but all have been proportional to temperature (by definition, the residual width described above is temperature independent). Yafet [120] first included localized moment spin-conduction electron orbit interactions into a dynamic relaxation calculation. The orbital motion of the conduction electrons is never bottlenecked, either because of the small number of electrons involved (see Hirst [121]) or because both impurity and phonon interactions are experienced by the electron orbital motion. Thus, the localized electron can flip its spin while the conduction electron changes its orbital state, relaxing to the bath instantaneously. An impurity lattice

relaxation rate proportional to  $T$  cannot be distinguished from a temperature independent conduction electron-lattice relaxation rate by virtue of (12). (The latter is multiplied by the ratio of the conduction electron susceptibility to the localized moment susceptibility. The inverse proportionality of the latter to  $T$  then results in a resonance width proportional to  $T$ ). Yafet finds [120], in fact, that  $\delta_{iL}$  simply enhances the effect of the conduction electron-lattice relaxation rate on the *EPR* linewidth by factors of two or three.

#### IV. THE FUTURE

It is always difficult to predict new directions for a field. We therefore restrict ourselves to future developments which, to us, appear as logical extensions of the work presented at Haute-Nendaz.

##### *Realistic treatment of the conduction electrons*

To the present, only free electrons, limited to a spherical Fermi surface, have been used in the calculation of the  $g$  shift and linewidth for *EPR* of dilute magnetic alloys. Exchange enhancement of the conduction electron susceptibility has been included, as well as separate  $s$  and  $d$  bands contributions, along with the wave vector dependence of the exchange. However, realistic band structures have yet to be introduced, leading to a certain amount of concern that the coupling parameters hitherto deduced from experiment may be meaningless. Reliable band calculations are now available for a variety of hosts which have been used in *EPR*, and atomic calculations for  $J(\vec{q})$  are becoming available for most transition metal and rare earth atoms. It is certainly appropriate to use the calculated value (it has already been done for *Pd*) for the  $\vec{q} = 0$  component of the conduction electron susceptibility to obtain  $J(\vec{q} = 0)$  from the  $g$  shift, and the wave vector dependent, imaginary part, of the conduction electron susceptibility for the linewidth. In the latter case, there will be a convolution of the susceptibility and wave vector dependent exchange which may make a reliable estimate of  $J(\vec{q})$  difficult.

To illustrate how important this procedure is, very recent work [25] on  $Mo_{7-x}Ga_{31}:Mn_x$  displays the following results: The exchange between the *Mn* and the superconducting conduction electrons is large and negative as deduced from the "compensation effect", leading to an increase in  $H_{c2}$  as the *Mn* concentration is increased. However, the magnetic resonance  $g$  shift is positive, and strongly dependent on temperature. The clear inconsistency between these results, when viewed against the consistency found for the "simpler" system  $LaRu_2:Gd$  [26], makes it clear that different electrons are predominantly involved in the superconductivity and magnetic resonance response of  $Mo_7Ga_{31}$ . Only an honest treatment of the conduction electrons can enable the beautiful complexity of this system to emerge.



There is another feature of the dilute magnetic alloy problem which needs a similar approach. The hyperfine interaction has already been shown to depend on the exchange-polarized conduction electron cloud in the vicinity of the magnetic ion. However, the exchange and host susceptibility important for hyperfine shifts are the local values (summed over all  $\vec{q}$ ), whereas the magnetic resonance  $g$  shift depends only on the uniform (or  $\vec{q} = 0$ ) component of the exchange and host susceptibility. There must be differences between these two products, but as yet nothing quantitative has been established.

### *Internal spin-spin fields*

It is now understood that, to avoid interaction effects, one must go to solute concentrations as low as 10 ppm [122]. It is interesting to reverse the trend, and to ask what happens as the concentration is gradually increased, thus "turning on" the spin-spin interaction field. Controllable effects have been seen in the fine structure of *Gd* resonances in *Au* and *Pd* hosts. In fact, this method (using spin-spin narrowing of fine structure) has the promise of enabling one to obtain the actual internal distribution of spin-spin fields in a dilute alloy. In comparison, specific heat measurements can only give information on the amplitude for zero internal field [123]. Resistivity is a difficult tool to use for the separation of single impurity from interacting impurity effects [124], and susceptibility experiments have so far provided only the effective moment and "Kondo" temperature of interacting pairs and triples [125].

A possible approach would be the following. At the lowest concentrations the fine structure exhibits well-separated lines characterized by the one-spin Hamiltonian appropriate to the local solute site symmetry. As the concentration is increased, the fluctuating field from other magnetic ions will be felt at the particular site, inducing spin flip transitions between, and shifts of, the various fine structure lines. The wings of the internal field distribution will first cause significant narrowing, but only at those sites which experience these extreme fields. This will lead to a partially collapsed spectrum superposed upon the resolved spectrum. The change in the observed fine structure spectrum can be traced back to a specific internal field distribution. The essential non-linear character of the narrowing process in the intermediate region allows one to separate the effects of the wings of the interaction distribution from the central peak.

Having the actual shape of the distribution may well produce some very interesting metallurgical conclusions regarding clustering or the formation of inter-metallic compounds. Indeed, the undoubted dependence of the internal spin-spin field distribution on sample preparation and handling may be just the tool to investigate ionic distribution questions at very low concentrations (10 to 1,000 ppm) where microprobe techniques are not feasible.

Unfortunately, there is no currently accepted theory for isotropic internal spin-spin fields, only an Ising model [126] which is expressed in a  $P(H)$ , the internal field distribution. Clearly, spin flips must be present, and indeed are essential for fine structure narrowing. Thus, *EPR* may be much more sensitive to the Heisenberg character of the spin-spin interaction than specific heat and magnetization experiments. A theoretical description of the internal interaction Hamiltonian in a random (or not-so-random) isotropic system, its strength and its distribution, is clearly needed.

### *EPR in the superconducting state*

A number of experiments under these conditions have been briefly mentioned in the text [26]. Gradually, we are amassing information which illustrates the character of the *EPR* signal (though so far only for *S*-state *Mn* and *Gd* dilute alloys). Single crystal alloys in which a resonance can be observed, and which are superconducting in a convenient temperature range, would be of immense value. Thus, given the anisotropy of the  $\Gamma_8$  field for resonance, one would only have to rotate the crystal or magnetic field to observe the *EPR* signal in (or out) of the superconducting region at constant field. At constant angle, the material could be brought into or out of the superconducting state (as  $H$  sweeps through  $H_{c2}$ ), and the magnetic resonance observed in either the superconducting or normal state, depending on the field for resonance at the particular angle, and on  $H_{c2}$ . It is also possible that at a given angle, the multitude of  $\Gamma_8$  lines might span  $H_{c2}$ , so that some could be observed in the superconducting state and others in the normal state at the same temperature.

The need for such experiments rests on our current lack of understanding of the temperature dependence of the *EPR* linewidth as one passes from the normal to the superconducting state. The  $g$  shift can be argued on the same basis as the Knight shift, but the linewidth of electron spins can hardly be attributed to spin diffusion to the vortex cores (as for *NMR*) at magnetic ion concentrations of 25 ppm. Very recent measurements of Davidov, Rettori and Kim [26] have exhibited a remarkable insensitivity of linewidth to concentration over the full measured temperature range (down to  $T_c/6$ ).

The local superconducting electron depairing in the vicinity of the paramagnetic impurity must have some effect on the *EPR* signal. For example, a large local reduction in order parameter could lead to local Fermi-like excitations similar to those proposed by Caroli de Gennes and St. James [127] for the vortex core. *EPR* then measure would the polarization and fluctuations of the local Fermi excitations. This is to be contrasted to *NMR* where spin diffusion is necessary to couple the nuclei to fluctuations of the vortex core. *EPR* gives one a local probe of the superconductor, while *NMR* gives results proportional only to a spatial average of the order parameter.

No theory which treats the dynamics of local excitations exists, though a start has been made by Kümmel [128] on the spatial variation of the order parameter itself. This is an exciting new area where experiment and theory can compliment one another in the process of untangling the physics of magnetism and superconductivity.

If the theory can be made tractable, then the number of possible investigations seems limitless. One can think of the *EPR* probe (remember that only 25 ppm of magnetic impurity are necessary) as being used in the same manner as "spin labels" in biology. When one wants to investigate the order parameter at a given point in a material (e.g. using the proximity effect to make superconducting thin films of normal dilute alloys), the shift and width of the *EPR* line could be used to obtain the local value. Exchange and spin orbit relaxation of the conduction electrons have differing temperature dependences in the superconducting state [129]. Thus, the influence of other ions, both magnetic and not, on the conduction electron dynamics could be detected by noting the temperature dependence of the *EPR*  $g$  shift and linewidth in the bottleneck regime below  $T_c$ . Other experiments come to mind. An example would be examining critical fluctuations near  $T_c$  by magnetic resonance in less-than-three-dimensional systems. Everything depends on the understanding of the influence of the "spin label" on the superconductivity of the host. Once this is understood, the prospects seem very exciting.

#### *Double bottleneck EPR*

The work of Hirst *et al.* [113] on *Cu* co-doped with *Mn* and *Cr* represents another very interesting new line of research in this area. For many reasons, including lattice relaxation or limited solubility, the direct magnetic resonance of a given ion may not be observable in a particular host metal. However, the very long range of the transverse dynamic response at resonance makes possible the simultaneous observation of more than a single species even in a material where the static Ruderman-Kittel coupling is of short range. It was discovered that the *Cr* resonance in *Cu*, though directly unobservable, was coupled with the *Mn* resonance and was itself bottlenecked. This led to a  $g$  shift of the combined (three spin species) resonance which allowed for a direct determination of the *Cr*  $g$  factor. Of course, the transmission measurements of Monod and Schultz [72] had already reported the *Cr*  $g$  factor, but there are many other alloys where transmission cannot work because of too short a spin lifetime (and therefore too short a spin diffusion length). When the additional ion is not bottlenecked, there will be a difficulty associated with the separation of exchange and spin-orbit relaxation of the conduction electron spin (e.g. *Cu:Fe*). However, systematics of the latter may help, and in any case upper limits on both can be obtained. Clearly, one of the more interesting experiments in co-doped materials would be the observation of the large increase in exchange spin-flip of the conducting electrons caused by the secondary impurity passing

through its Kondo temperature. One can even conceive of passing from a bottlenecked to a non-bottlenecked response as the temperature is lowered, because of the Kondo effect. This situation would have a unique signature, and would allow for quantitative determinations of conduction electron dynamics in the vicinity of the Kondo impurity. This is similar to the re-entrant behavior of Kondo superconductors recently reported, but applies here to the normal state [130].

*Extrapolation to concentrated materials*

The complete specification of the local, or one ion, characteristics, and some understanding of the systematics in going from the dilute to the concentrated regime, should enable one to work with a much more accurate Hamiltonian when investigating collective excitations in the concentrated material. A case in point is the rare earth metals, where exchange and crystal fields combine to give an excitonic excitation spectrum directly observable in neutron diffraction. The specification of the exchange coupling has to date been very primitive, with workers only recently recognizing the importance of anisotropic exchange [131]. *EPR* (e.g. *Pd:Dy*, [30]) can yield the full anisotropy of the exchange, as well as the magnitude and sign of the crystal field parameters. By making *EPR* measurements in, say, *Sc*, or some other non-magnetic host with energy bands resembling the rare earths, values for these parameters could be extracted which could then serve as a starting point for the analysis of the concentrated rare earth system. At present, no unique information is available with which to make comparisons, and the anisotropy of exchange used in fitting the rare earth spin wave spectrum may not be unique. Similar remarks can be made with respect to the crystal field splittings. They tend to become convoluted with exchange (especially in the heavier rare earth metals) and independent determinations in non-magnetic hosts of similar band structure would be of great value.

In summary, the unscrambling of single ion *EPR* spectra for dilute magnetic alloys has pointed to a number of new and exciting paths for future development. Not only can the magnetic ion be studied to learn more about its own behavior, but it can also be used as a probe to exhibit the physical properties of the host. The field has become immeasurably more interesting as the physics which can be investigated becomes more rich. *EPR* in metals has reached the point where it can be used as a tool for the investigation of the physics of metals.

TABLE 1

*Historical development of EPR of Impurities in Metals ; mainly experimental*

- 1954 First observation of EPR in metals: *Gd* metal (a)  
 1956 EPR of *Mn* in *Cu Ag & Mg* (b)  
 1959 Hasegawa's Theory (c)  
 1962 Correlation between *g* shifts and electronic susceptibility in metals. Long range interaction of R.E. in *Pd* (d)  
 1966 Observation of non *S*-state rare earth ions in metals:  $\Gamma_7$  (e)  
 1967 Experimental investigations of Hasegawa's Theory, the bottleneck problem (f)  
 1967 Anisotropy measurements in single crystals: *Er* in *Mg* (g)  
 1970 Observation of hyperfine interactions (h)  
 1971 Observation of fine structure in *Gd* in *Mg* (i)  
 1972 Observation of  $\Gamma_8$  in single crystals (j)  
 (a) A. F. KIP, C. KITTEL, A. M. PORTIS, R. BARTON and F. H. SPEDDING, Phys. Rev. 89, 518 (1953)  
 (b) Reference 1.  
 (c) Reference 3.  
 (d) Reference 11 and 12.  
 (e) Reference 2.  
 (f) Reference 6 and 7.  
 (g) Reference 43.  
 (h) Reference 40.  
 (i) Reference 44.  
 (j) Reference 47 and 48.

TABLE 2

*Ground state of Er in various fcc metals ; Possible assignments of W and x*

Metal	Ground State	Point Charge Model			Other Possibility		Reference
		W	X	Sign	W	X	
<i>Al</i>	$\Gamma_7$	+	+	+	+	—	a
<i>Cu</i>	$\Gamma_7$	+	+	+	+	—	b
<i>Rh</i>	$\Gamma_7$	+	+	+	+	—	c
<i>Pd</i>	$\Gamma_8^{(3)}$	—	+(.47)	—			d
<i>Ag</i>	$\Gamma_7$	+	+	+	+	—	e
<i>Ir</i>	$\Gamma_7$	+	+	+	+	—	f
<i>Pt</i>	$\Gamma_6$	—	+	—	+	—	g
<i>Au</i>	$\Gamma_7$	+	+	+	+	—	h
<i>Th</i>	$\Gamma_7$	+	+	+	+	—	i

- a. C. Rettori, D. Davidov, R. Orbach and E. P. Chock, Phys. Rev. B7 1 (1973).  
 b. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. J. Tao, Phys. Letters 35A 339 (1971).  
 c. Reference 19.  
 d. Reference 46.  
 e. References 2 and 40.  
 f. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. J. Tao and B. Ricks, Phys. Letters 37 A 361 (1971).  
 g. Reference 19.  $\Gamma_6$  is the proper ground state.  
 h. Reference 41.  
 i. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel and L. J. Tao, Phys. Rev. 85 1711 (1972).



TABLE 3

*Ground state of Dy in various fcc metals and possible assignments of x and W*

Metal	Ground State	Point Charge Model			Other Possibility		Reference
		W	X	Sign	W	X	
<i>Al</i>	$\Gamma_7$	+	—	+	+	+	a
<i>Rh</i>	$\Gamma_7$	+	—	+	+	+	b
<i>Pd</i>	$\Gamma_8^{(3)}$	—	— (— .55)	—			c
<i>Ag</i>	$\Gamma_7$	+	—	+	+	+	d
<i>Ir</i>	$\Gamma_7$	+	—	+	+	+	e
<i>Pt</i>							f
<i>Au</i>	$\Gamma_8$				+	+(.85)	g
<i>Th</i>	$\Gamma_7$	+	—	+	+	+	h

- a. C. Rettori, D. Davidov, R. Orbach and E. P. Chock, Phys. Rev. B 7 1 (1973).  
b. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. J. Tao and B. Ricks, Phys. Letters 37A 316 (1971).  
c. Reference 48.  
d. D. Davidov, R. Orbach, L. J. Tao, E. P. Chock, Phys. Letters 34A 379 (1971).  
e. D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. J. Tao and B. Ricks., Phys. Letters 40A 269 (1972).  
f. Not observed in powders see text.  
g. Reference 47.  
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TABLE 4

*Sign of crystal field parameter of Er and Dy in Ag, Au, Pd and Pt*

	$C_4$	$C_6$
<i>Ag, Au</i>	—	+
<i>Pd, Pt</i>	—	—
Positive point charge	+	+

$$B_4 = C_4\beta \quad B_6 = C_6\gamma$$

## APPENDIX 1

*List of host elements and ion impurities whose resources were measured with the references.*

Impurity Ion	S state ions			Non S state ions		
Host element	<i>Mn</i>	<i>Gd</i>	<i>Eu</i>	<i>Dy</i>	<i>Er</i>	<i>Yb</i>
<i>Mg</i>	a	b			c	
<i>Al</i>		d		d	d	
<i>Ca</i>			e			
<i>Sc</i>		f				
<i>Cu</i>	a	g			h	
<i>Y</i>		i				
<i>Rh</i>		j		k	j	
<i>Pd</i>	l	m		n	o	
<i>Ay</i>	a	p		q	r	
<i>La</i>		s				
<i>Ce</i>		t		t	t	
<i>Yb</i>		u	v			
<i>Lu</i>		w				
<i>Ir</i>		x		x	x	
<i>Pt</i>		j			j	
<i>Au</i>		y		z	h	A
<i>Th</i>		B		B	B	

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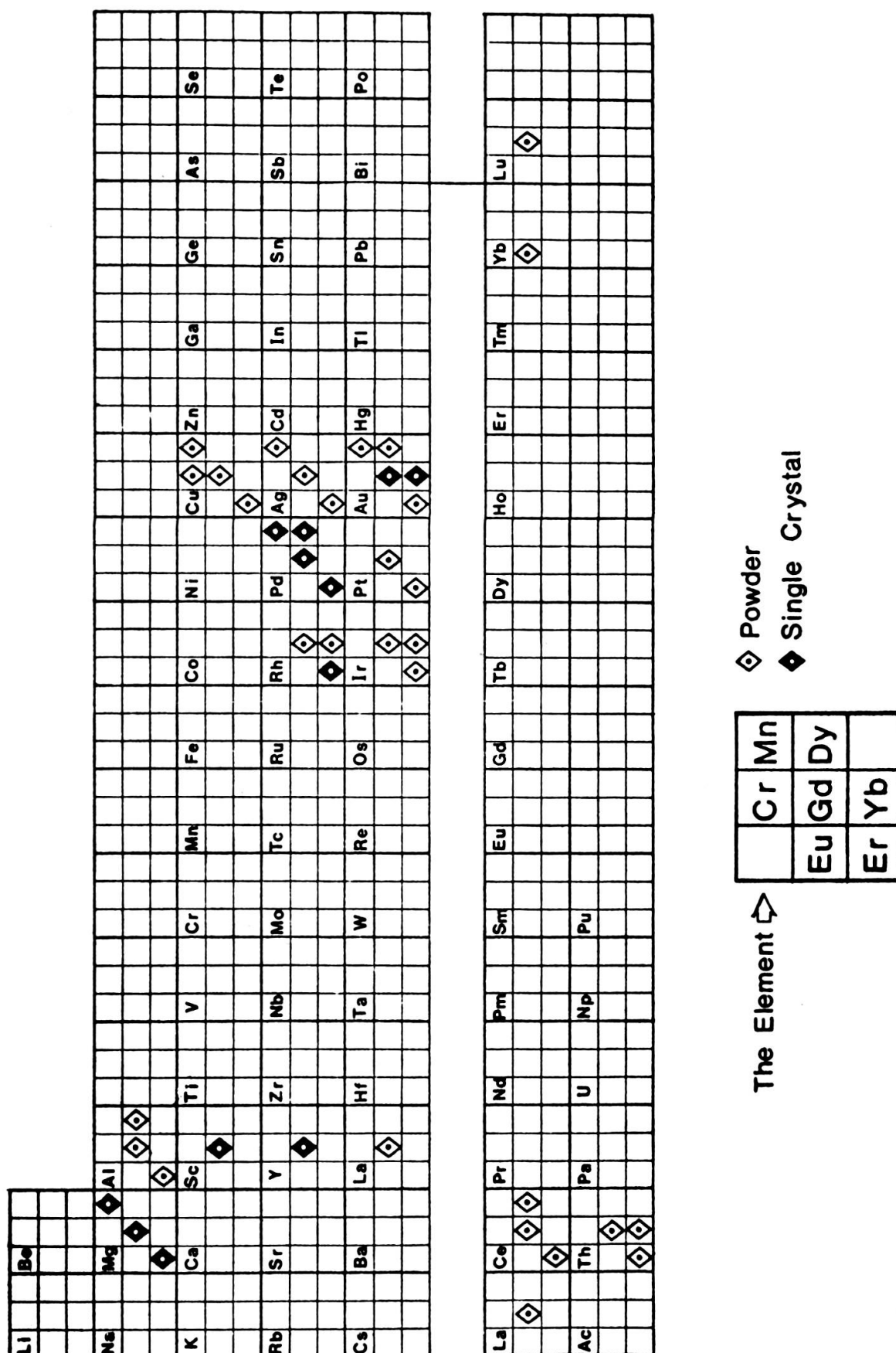


FIG. 1. — The magnetic impurity ions whose *EPR* has been measured in elemental host metals, are exhibited diagrammatically on the periodic table.

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## DISCUSSION

YAFET: *Gd* is not bottlenecked in *Pd*; it is an *S*-state ion. Can you understand why it is not bottlenecked?

SHALTIEL: Well, I think it is that the *d* electrons are very effective in the relaxation processes.

WILKINS: What about doing transmission spin resonance in pure *Pd* for instance? That has not been blessed with total success—am I right? I am just hoping that someone is going to raise their hand and say: “no—we have done it in our lab...”

KAPLAN: I think people tried...

WILKINS: I know they have tried!

(Voice): Well, that is a good experiment for a theorist!

WILKINS: May be should not expect a bottleneck. If for a variety of reasons which we can try to discuss at some stage you do not see transmission spin resonance in *Pd*, may be you should not expect a bottleneck to occur when you put *Gd* into the *Pd* for instance.

ORBACH: I do not think there is any suggestion that there is a bottleneck here. If there were a bottleneck in this material it would be the first one we have ever seen in a transition metal.

PETER: What happened is that people fall, as we did with the *Pd*, on something that is apparently not bottlenecked. Then that is precisely the kind of thing where you can go with reasonably high concentrations to look at the ions and it is precisely the kind of thing where you have no luck with the transmission technique. Because the fact that it is not bottlenecked means there is a very rapid relaxation of the conduction electrons and therefore the transmission technique is not applicable. So why not accept for the time being that *Pd* is a case which is not bottlenecked, where we did not lose anything by not doing transmission and where we won a lot doing it the other way, because we did not get wrong results by ignoring the bottleneck.

MONOD: There is one thing I do not quite understand in the fine structure narrowing. I understand you have a mechanism which you call an internal mechanism between these different levels that do not involve exchange to the conduction electrons...

ORBACH: It involves the spin-flip of the localized spin caused by the exchange coupling with the conduction electrons, but it is not coupled to the conduction electron magnetization in the way that the bottleneck term is. The width that we spin flip to, by the way, is exactly the width calculated by Hebel and Slichter in the total absence of fine structure. The narrowed width has no dependence on *D* and no dependence on *S* or *S<sub>z</sub>*. It is simply given by  $\pi [JN(E_F)]^2 kT/\hbar$ . At low temperature that is much narrower than the full fine structure splitting.

KAPLAN: Is the bottleneck essential to have this narrowing ?

ORBACH: No, the bottleneck is not essential to reach the Hebel-Slichter limit, but to get from that limit down to the observed width it is necessary to turn on the bottleneck. There is an intermediate régime where you can have a bottleneck but still have resolved fine structure. I have given you the process where first you narrow the fine structure and then you turn on the bottleneck by turning off the spin relaxation of the conduction electrons. But you can have the opposite happenig. You can have each of the fine structure lines separately bottlenecked but the fine structure not collapsed. You must have very special conditions for that to occur. If that happens Plefka and Barnes have shown that the line-width of each of the fine structure components is not given by the usual Korringa rate, but includes a factor depending on  $S_z$ .

TAYLOR: We have been doing powder work on  $Gd$  in  $Pd$  recently and we are in agreement that at concentrations far less than  $1/4\%$  there seem to be very significant interaction effects. We have seen this by virtue of the fact that the linewidth broadens and the resonant frequency shifts, and in some cases this is at several times the Curie temperature for the material. This also seems to be true in a wide range of intermetallic compounds that we have studied. It would appear that *EPR* is a very good tool for showing up the effects of interactions, and I think that some sort of short range order effects are probably the cause.

Another thing is that in this work, there seems to be a strong frequency dependence of the residual linewidth. It seems to go roughly as the square root of the measuring frequency or fields. Is there anything you can see from your fine structure work which could give rise to a frequency dependent effect ?

ORBACH: I cannot think of anything. We evaluate our self-energies at the resonant frequencies.

WILKINS: So therefore you could say how much they shift with a change in resonant frequency.

ORBACH: But it is not there; it cancels out.

SHALTIEL: A small comment on the residual linewidth. We were able by some metallurgical techniques to reduce the residual linewidth by a factor of four, and so therefore I would say that a large part is a question of metallurgy.

DAVIDOV: But different concentrations give different  $g$  values. The  $g$  value you extract is basically the centre of a distribution of many different concentrations and hence  $g$  values. If you have a distribution of  $g$  values you expect a frequency dependence immediately because the sample is inhomogeneous. At UCLA they went to as low frequencies as possible just so as to observe the residual width.

