ESR AND ELECTRONIC STRUCTURE OF TRANSITION ELEMENT COMPOUNDS

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ABSTRACT

ESR spectra of localized moments are influenced by line broadening or splitting mechanisms like dipole- or hyperfine interaction etc. and narrowing effects due to motion in the spin system. This paper reviews and discusses motional and exchange narrowing in nonstoichiometric transition element bronces and in some europium and gadolinium compounds of simple cubic crystal structure which are often called magnetic semiconductors. The *ESR* spectra can be correlated with aspects of the electronic structure of these conducting compounds like motion of localized *d*-electrons or interaction between localized and conduction electrons.

I. INTRODUCTION

Compounds like chalcogenides, or pnictides etc. of the $3d$, $4d$, $4f$ ions, show an immense variety of electronic properties. Among them there are insulators like the often discussed NiO as well as metallic conductors like some of the tungsten oxides, ReO_3 or certain RE chalcogenides and many semiconductors [1, 2].

Important parameters which determine the electronic properties of these compounds are their stoichiometry and the nominal valence of the ions.

Let us consider a compound of the type $T^{2+}X^{2-}$ (T = transition element, X = anion group). The valence band, mainly formed by the X-ions is filled up by the two electrons of the bivalent transition element, this compound is usually thought to be an insulator, although there are some exceptions.

In the corresponding compounds of the trivalent ion $T'^{3+}X^{2-}$ the additional electron can occupy a conduction band. The mixed compound $T_{1-x}^{2+}T_x'^{3+}X^{2-}$, therefore, is generally an insulator for $x = 0$, and should be a metallic compound for $x = 1$ with one conduction electron per T ion.

Compounds of the nominal type $T_a^{w+}X_b^{w-}$ (a, b = integer, w means the valence) show a similar behavior if further ions can take up certain,

here unoccupied sites. Generally, this compound is an insulator. But compound type $M_x(T_{1-x}^{w+}T_x^{(w-1)+})_aX_b^{w-}$ — M means other additional ions on certain non T-sites—shows x charge carriers.

The behaviour of these additional change carriers (their density usually amounts to $0 < x < 1$ electrons/T-lattice site) is determined by interactions like [1]

electron correlations,

interaction with other localized electrons resp. their magnetic moments,

interactions with phonos,

interactions with nonperiodic Coulomb fields which are caused by the substitution of M ions or by statistical occupation of the lattice sites by T ions of different nominal valence.

The character of the electronic conduction in these compounds with $0 < x < 1$ depends on the extent of localization of the additional charge carriers due to these effects.

Interactions of localized electrons like crystal field-, hyperfine field-, dipole field interactions or statistical distributions of the resonance field due to disorder effects etc., influence ESR spectra of these compounds in such a way as to cause a splitting or an inhomogeneous broadening of the ESR transition. Motion of electrons or motion in the spin system like isotropic exchange can lead to a line narrowing due to time modulation of these broadening mechanisms.

This report deals especially with the effects causing a motional or exchange narrowing of the ESR lines in certain simple transition element compounds. Usually, the difficulties, to interpret narrowed ESR linewidths are caused by the problem of spin correlation functions. Therefore the observed narrowing effects are discussed only in a phenomenological and qualitative way and only a comparison of these experimental results with certain aspects of the electronic structure of these compounds is given.

In the first part simple models of motional narrowing effects in transition element bronces are considered, in the second part exchange narrowing in some Eu and Gd compounds of simple cubic crystal structure, which are often named magnetic semiconductors.

II. MOTIONAL NARROWING EFFECTS
IN TRANSITION ELEMENT BRONCES

Oxides like V_2O_5, MoO_3, WO_3 etc., generally T_aO_b, are diamagnetic insulators (fig. 1). The d levels of the transition ions are unoccupied. The crystal structure consists of more or less distorted TO_6 octahedra. An interesting feature of these

compounds is the fact that certain sites between octahedra can be occupied by additional metal ions M like Na^+, K^+, etc. In these $M_xT_aO_b$ compounds, named transition element bronces, x d-electrons can be found within the TO_6 octahedra. They achieve the charge compensation of the M ions.

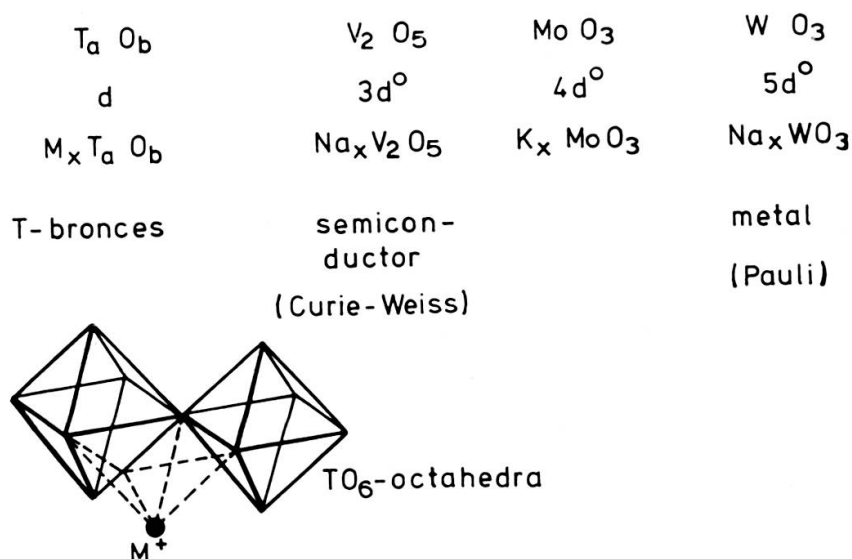| T_a O_b	V_2 O_5	Mo O_3	W O_3
d	$3d^0$	$4d^0$	$5d^0$
$M_x T_a O_b$	$Na_x V_2 O_5$	$K_x Mo O_3$	$Na_x WO_3$
T-bronces	semicon-ductor (Curie-Weiss)		metal (Pauli)

TO_6-octahedra

M$^+$

FIG. 1. — Review of different transition element bronces M_x T_a O_b

It can generally be said (fig. 1) that most of the vanadium bronces are semiconductors, while the tungsten bronces are metallic compounds. The mechanisms which cause a localization of the $3d$ charge carriers on certain vanadium lattice sites are much more effective than in the case of $5d$ electrons. The behavior of $M_x MoO_3$ depends on the kind of the M ion and on the x value. These compounds show metal-semiconductor-transitions.

Let us first turn to the semiconducting V_2O_5 systems. Conductivity measurements, performed by various authors [3, 4, 5], result—if V_2O_5 is slightly doped—in two activation energies, about $0.07\,eV$ at $T \gtrsim 200\,K$ and about $0.25\,eV$ at $T \gtrsim 200\,K$. It is extremely important to find out whether the exponential temperature dependence of the electric conductivity is determined by the mobility or the concentration of the charge carriers. That means whether hopping processes of localized electrons or band conduction of delocalized electrons occur.

Localized d electrons can be examined by ESR. Figure 2 shows the ESR spectrum of semiconducting V_2O_5 with 1% Na ($Na_{0.01}V_2O_5$) at a temperature of $100\,K$ for $H_0 \parallel$ the crystallographic b-axis which coincides with the magnetic z-axis. A resolved HFS is found which can be interpreted by equal interaction of one $3d$ electron with four vanadium nuclei ($I = \dfrac{7}{2}$). This resolved structure disappears

with increasing temperature. At first an inhomogeneously broadened line remains. Then it narrows with increasing temperature, its shape becomes Lorentzian.
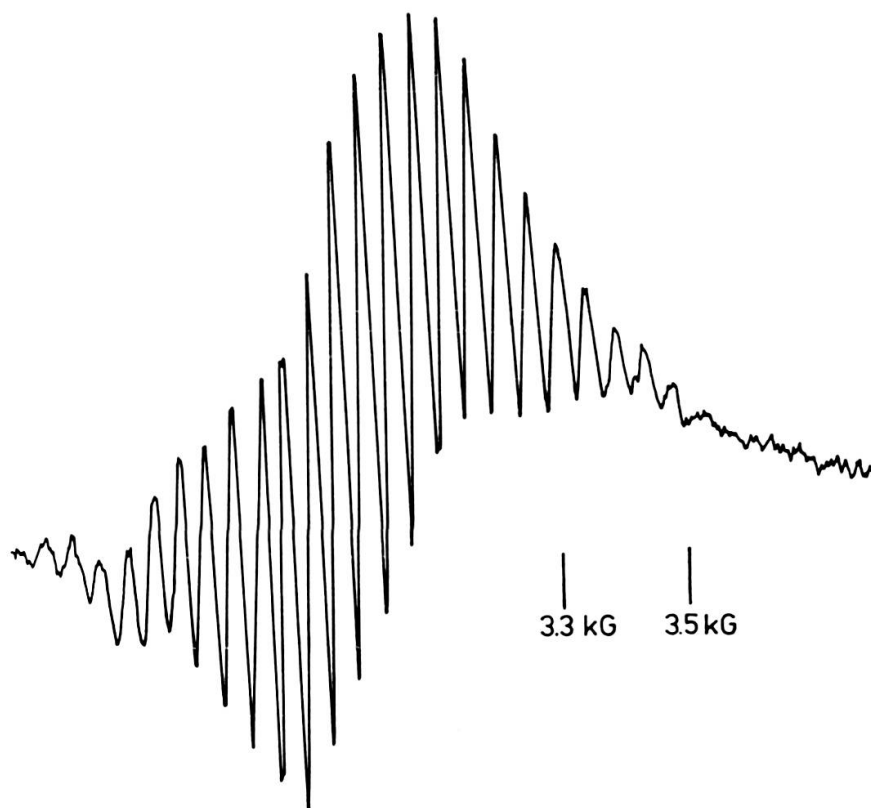

FIG. 2. — *ESR on* $Na_{0.01}V_2O_5$; $H_0 \parallel b$-axis = magnetic z-axis; $T \approx 100 \ K$; $\nu \approx 9.5 \ GHz$

Figure 3 shows the temperature dependence of the linewidth for several orientations of the magnetic z-axis to the external magnetic field in the range where no more resolved *HFS* occurs. A line narrowing is observed. In the range above room temperature a gradual broadening takes place.

HFS tensor, g-tensor, the *ESR* linewidth etc. yield information about the paramagnetic properties, the bonding mechanisms, etc. [6, 7]. From the line narrowing we want to learn something about the motion of the d-electrons.

At first let us discuss the resolved *HF* splitting. Due to the additional *M*-ions, there are nonperiodic Coulomb fields in the V_2O_5 crystal. The energy difference of neighboring d-levels in the vicinity of the *M* ions becomes larger than the width of the narrow "$3d$-bands". This results in the so-called Anderson-localization of the d-electrons [9]. Every Na^+-ion of the V_2O_5 matrix is immediately surrounded by four VO_6 octahedra. The $3d$ electron remains mainly delocalized over this four vanadium sites. The interaction with the four V^{51} nuclei with nuclear spin $I = \dfrac{7}{2}$ causes the intensity distribution of the observed 29 *HFS* lines of figure 2.

This conclusion is confirmed by *ESR* measurements on the related V_2O_5 compounds:

$$(V_{1-x}Mo_x)_2O_5 \quad \text{and} \quad (V_{1-x}W_x)_2O_5 \quad \text{with} \quad x = 0.005 - 0.01.$$
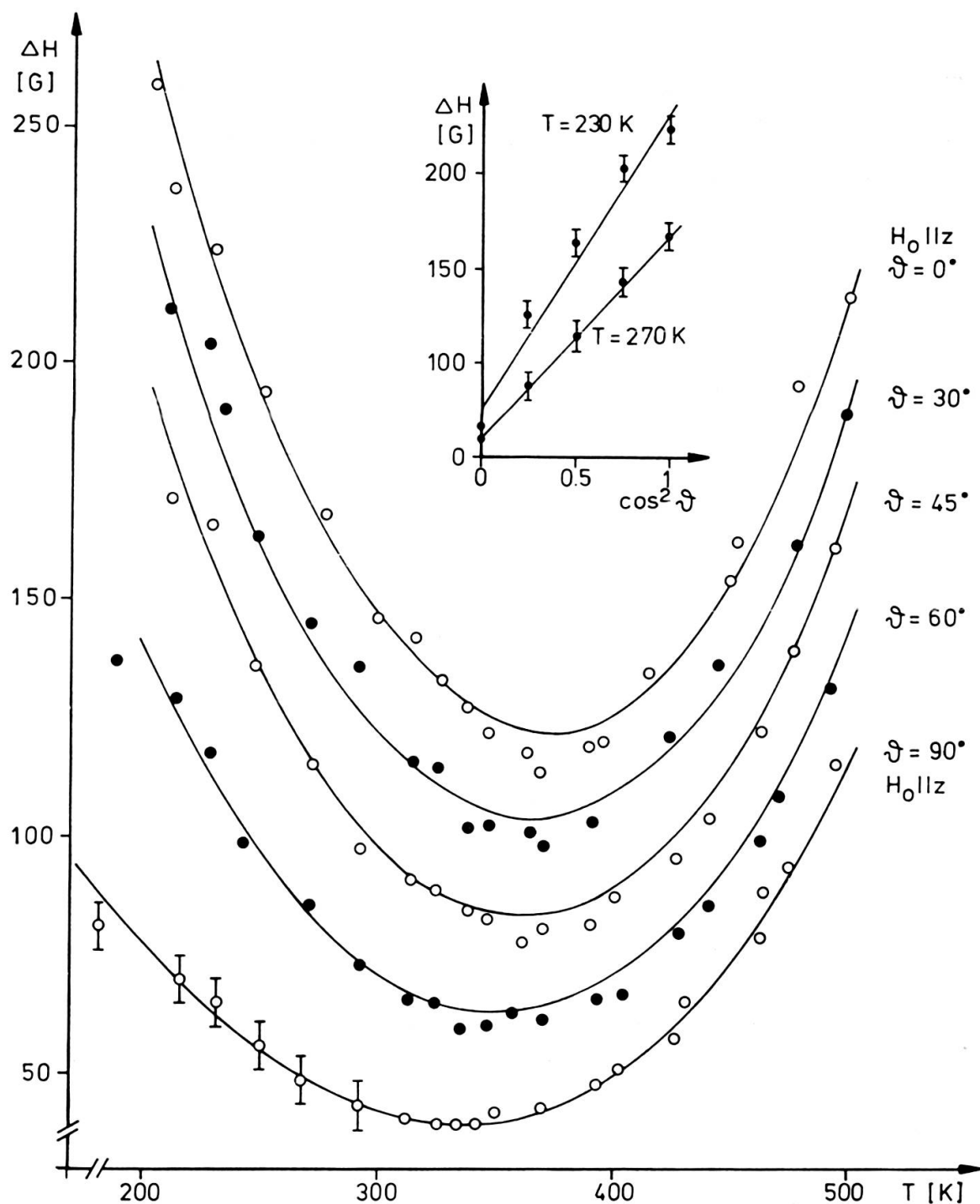

FIG. 3. — Temperature- and orientation dependence of *ESR* linewidth ΔH for $Na_{0.01}V_2O_5$ in the magnetic *z-x* plane;
000000   measured
————   calculated;
$\nu = 9.0 \, GHz$; $\vartheta =$ angle (H_0, z)

In contrast to $Na_xV_2O_5$ where the monovalent Na^+ ions occupy interstitial sites, the hexavalent Mo^{6+}- or W^{6+} ions substitute the pentavalent vanadium ions. This effect causes a redistribution of the nonperiodic Coulomb fields. In these crystals only one neighbouring vanadium site is energetically preferred. That means, one should expect a *HF*-interaction of the 3*d*-electron with only one nuclear spin $I = \frac{7}{2}$ with a four times larger coupling constant than in the case of $Na_{0.01}V_2O_5$.

The observed *ESR* spectrum with the expected 8 *HFS* lines is plotted in figure 4 for two orientations of the crystal. A discussion of further details like orientation
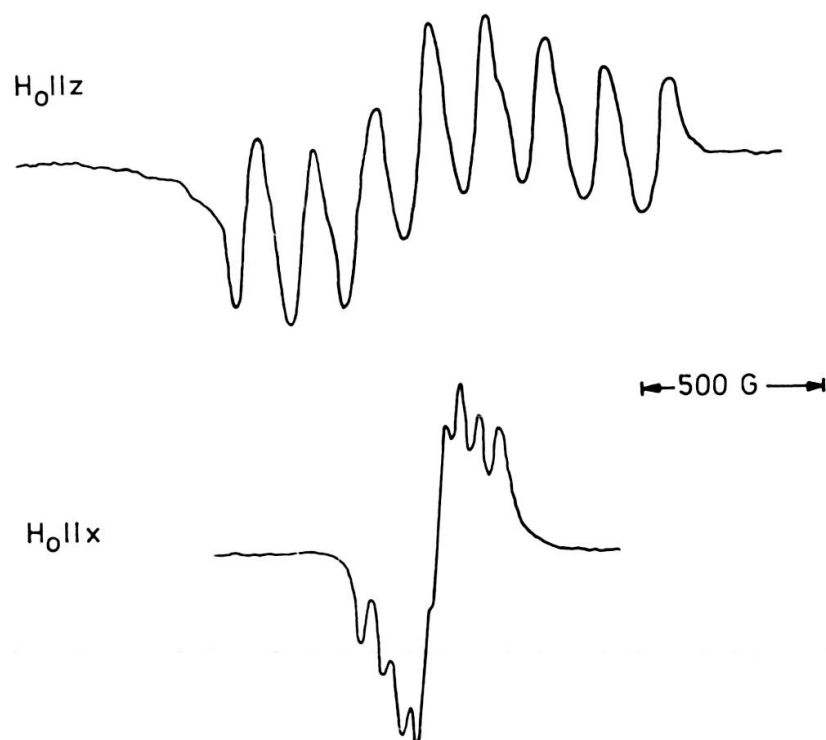
FIG. 4. — *ESR* on $(V_{1\text{-}0.01}W_{0.01})_2O_5$ single crystals;
$H_0 \, || \, z$ and x axis; $T = 120 \, K$; $\nu \approx 9.5 \, GHz$

dependence, linewidth, etc. and the interpretation of *ESR* signals on V_2O_5 with other dopants confirms the mentioned model. A line narrowing similar to the one of $Na_{0.01}V_2O_5$ occurs also in this crystal $(V_{1-x}Mo_x)_2O_5$ and $(V_{1-x}W_x)_2O_5$ at higher temperatures.

Now let us discuss the line narrowing effects.

In figure 5 we find a schematic diagram of the band structure. The valence band consists mainly of oxygen orbitals. Below the conductor band we have the above discussed localized or slightly delocalized *d*-electron states. In order to understand the occuring line narrowing effects, the following mechanisms shall be considered:

a)

$$\nu_e(T) \sim \exp\left(-\frac{E_a}{kT}\right)$$

$$\Omega(T) \sim \exp\left(-\frac{W}{kT}\right)$$

b)

c)

$$I(V) = -\text{Re } \underline{W} \ \underline{\underline{A}}^{-1} \ \underline{1}$$

$$\underline{\underline{A}} = \begin{pmatrix} i(V-V_1)-\frac{7}{8}\nu_e-\Omega-\delta & & \frac{\nu_e}{8} & \cdots & \frac{\nu_e}{8} \\ & \frac{\nu_e}{8} & & & \\ & \frac{\nu_e}{8} & & & \\ & & & & i(V-V_8)-\frac{7}{8}\nu_e-\Omega-\delta \end{pmatrix}$$
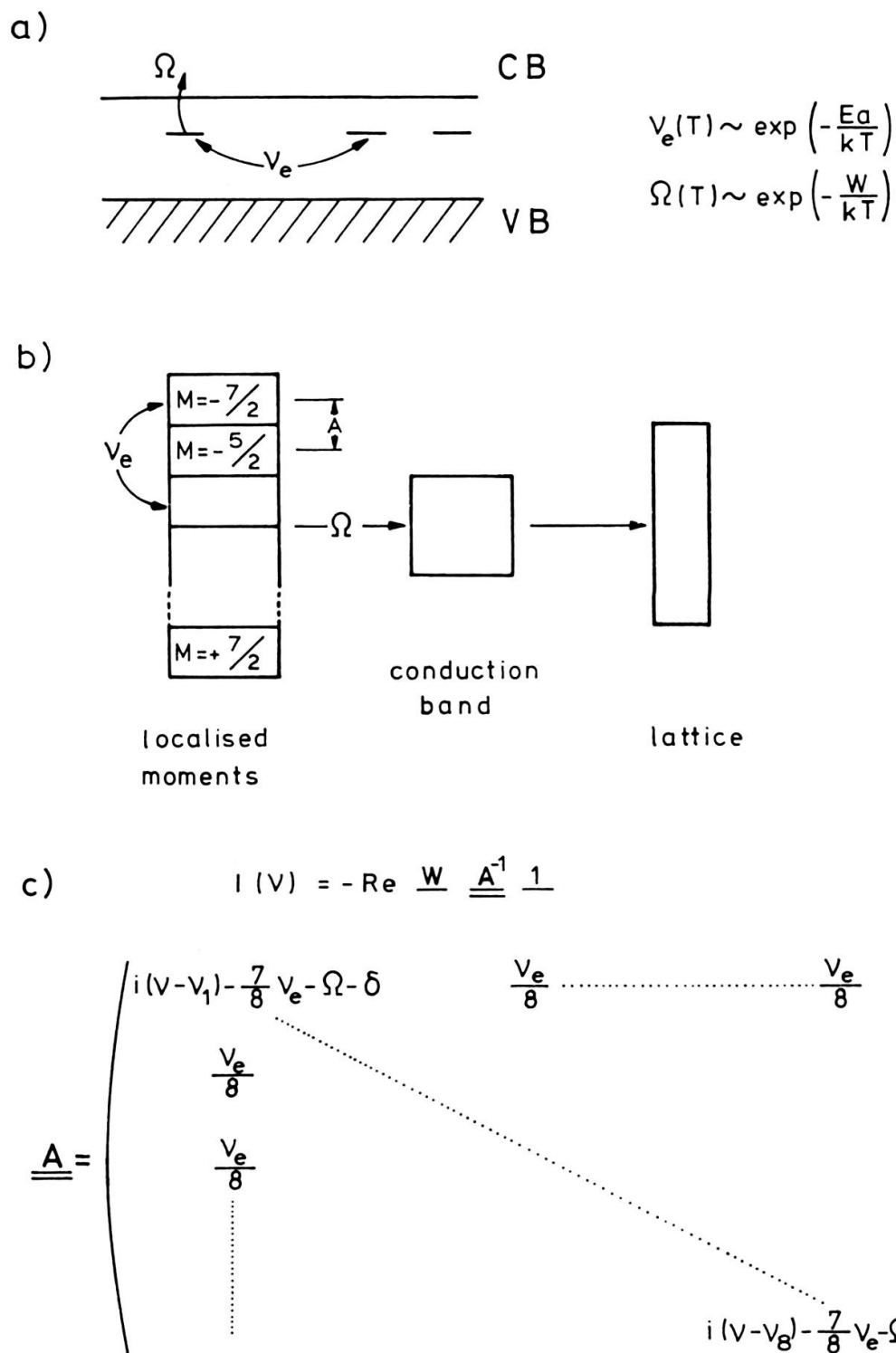
FIG. 5. — Model for mobile d-electrons, hopping frequency ν_e,
excitation frequency Ω, direct spin lattice
relaxation rate neglected;

    a) schematic band structure

    b) relaxation mechanisms

    c) Anderson formalism

1. A hopping process between the discussed localized states. The hopping frequency be expressed by the relation $v_e \sim \exp(-E_a/kT)$

2. Excitation into some form of conduction band in which a complete delocalization takes place. The excitation frequency be $\Omega \sim \exp(-W/kT)$.

These processes fit into a scheme which explains the temperature- and orientation dependence of the narrowed *ESR* signal.

The transfer process of the localized *d*-electrons on vanadium lattice sites causes a hopping between the different hyperfine structure lines in analogy to the mentioned process of exchange narrowing of *ESR* features in diluted magnetic alloys. The excitation of the *d*-electrons to the conduction band results in an effective shortening of the life time and, thus, in a broadening of the lines, provided the relaxation from conduction band to lattice is faster than a back relaxation.

A calculation of the *ESR* spectrum I (v) within such a model is possible, assuming a Markoff process for the time modulation of the *HFS*. The following relation for the measured spectrum I (v) is given by Anderson [10]:

$$I(v) = -Re\ \underline{W}\ \underline{\underline{A}}^{-1}\ \underline{1}.$$

$\underline{W}$ in this case means a line vector representing the probability of the occurence of $2I + 1$ *HF* components; $\underline{1}$ a unit vector. Matrix $\underline{\underline{A}}$ whose inverse is to be formed here, has in the case of 8 *HFS* lines the form of figure 5.

The off-diagonal elements indicate the probability of a hopping $v_e(T)$ between the single *HFS* lines, the diagonal elements contain the 8 *HFS* resonance frequencies v_i, and—as real elements—the line broadening mechanisms direct: direct spin lattice relaxation δ, and excitation frequency to conduction band $\Omega(T)$. This matrix becomes correspondingly more complicated for 29 *HFS* lines of different relative intensity. In the following three cases the solution for $I(v)$ is immediately given:

1. hopping frequency $v_e(T) \ll$ coupling constant A:
   discrete *HFS* lines occur [8].

2. $v_e(T) \gg A$ and negligible relaxation rate $\Omega(T) + \delta$:

   The line narrows with increasing T, the linewidth is given by $\Delta H \sim \dfrac{A(\vartheta)^2}{v_e(T)}$

   This relation is fundamental for the discussion of motional and exchange narrowing. The linewidth of the Lorentzian line is proportional to the second moment of the broadening mechanism—here the hyperfine interaction—divided by a hopping or exchange frequency. The orientation dependence of the coupling constant $A(\vartheta)$ causes the observed orientation dependence of the linewidth ΔH.

3. $v_e(T) \gg A$ but large $\Omega(T) + \delta$:

   The *ESR* linewidth is determined by the relaxation effects. It broadens with increasing temperature.

A related problem of line narrowing in the case of $TiO_2 : Nb$ is discussed in [11]. We have mainly two parameters at our disposal, namely the activation energies E_a and W. There are still some unsolved problems concerning the x-dependence of these parameters. But our numerical values for $Na_{0.01}V_2O_5 - E_a \sim 0.05\,eV$ and $W \sim 0.28\,eV$—correspond fairly well with the two values of the activation energy of the electric conductivity.

From these measurements on $Na_{0.01}V_2O_5$, therefore, we can derive that the activation energy of the electric conductivity at lower temperatures is determined by a hopping process—similar to impurity-impurity conduction. At higher temperatures some form of band conduction dominates.

We observed motional narrowed *ESR* lines in many V_2O_5 and MoO_3 compounds, and similar interpretations of the results were possible. As another, perhaps more interesting example, the mixed crystal $V_2MoO_8 = V_2O_5 . MoO_3$ should be mentioned.

The crystal structure consists of distorted TO_6 octahedra which are occupied by the vanadium and molybdenum ions in a nonperiodical way [12]. That means, although we perform *ESR* measurements on single crystals the statistical distribution of the transition ions on the lattice sites causes this system to behave similarly to an amorphous one.

Figure 6 shows the linewidth of the *ESR* signal as function of temperature between $3.8\,K$ and $300\,K$ for several orientations of the magnetic z-axis to the external magnetic field. The orientation dependence of the *ESR* linewidth and the g-factors are typical for $3d$-electrons.

A line narrowing due to a temperature dependent motion of the d-electrons and a homogeneous linewidth due to shortening of the lifetime of the localized electrons are also observed. These results have to be evaluated similar to those of $Na_xV_2O_5$.

Summing up, it can be said that in these compounds:

1. d-electrons appear due to controlled non-stoichiometry;

2. nonperiodic Coulomb potentials influence the band formation;

3. line narrowing effects in the *ESR* spectrum can be interpreted as motional narrowing of the *HF* structure due to the temperature dependent mobility of these d-electrons;

4. the homogeneous linewidth is determined by exitation of these d-electrons to a conduction band.

These results were proven in all examined $M_xV_2O_5$-bronces.

Some measurements were performed in the transition element bronces $M_xT_aO_b$ to clarify the role of the M-ions. In the ESR spectra of the d-electrons in $Na_xV_2O_5$
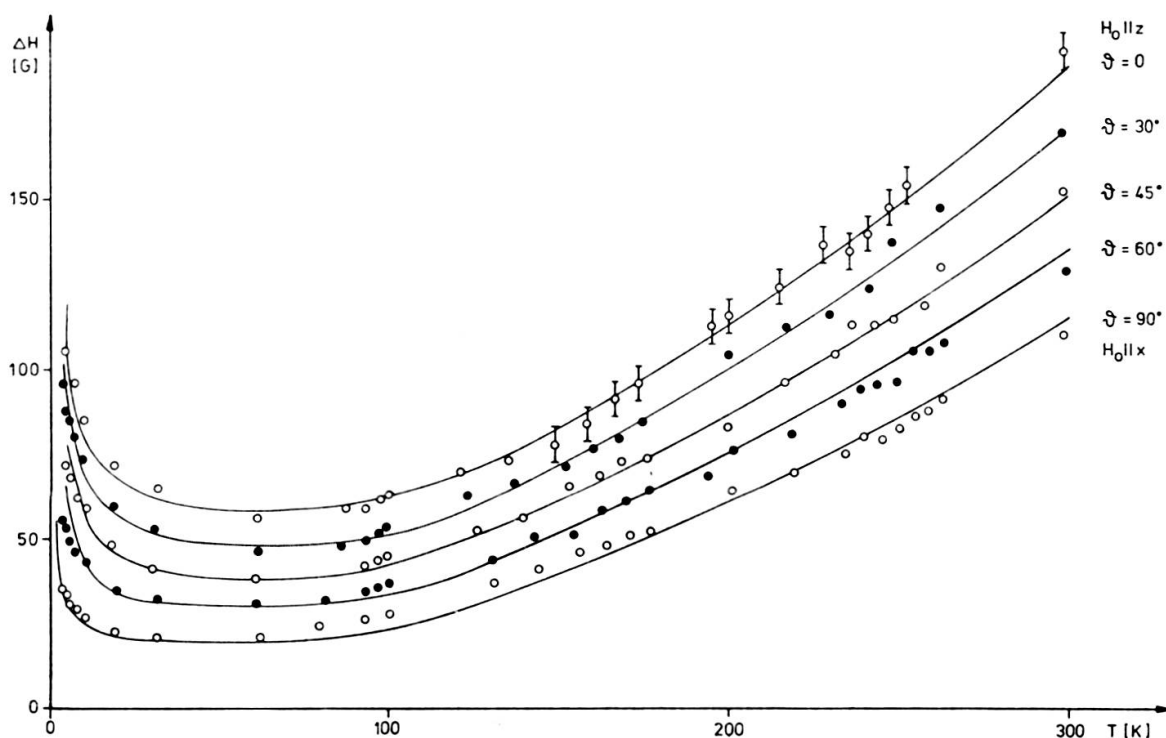

FIG. 6. — ESR on V_2MoO_8; temperature- and orientation dependence
of the linewidth in the z-x plane;
000000   measured
————   calculated;
$\nu \approx 35\ GHz$; ϑ = angle (H_0, z)

no splitting is observed which could be interpreted as $SHFS$ due to interaction with the Na-nucleus. ESR measurements on molybdenum bronces K_xMoO_3 were done by G. Bang [13], they yield similar results, no $SHFS$ by interaction of the $4d$-electron with potassium nucleus.

A similar effect takes place even in the metallic M_xWO_3-bronces. From NMR-measurements on the metallic tungsten bronces Na_xWO_3, Tl_xWO_3, published in [14], we know, that there is no measurable Knight shift at the M-site.

The role of the M-ions seems to be the following one: The valence electrons of the M-ion are added to the d-band. But the orbitals of the M-ion do not take part in the formation of the conduction band within the T_aO_b lattice. The M-ions behave like free ions.

We performed ESR measurements on the metallic M_xWO_3-bronces with RE-ions like La and Gd as M-ions. The results are consistent with this model of free Gd-ions within a metallic matrix.

The tungsten bronces $M_x WO_3$ have the ideal perovskite structure ABO_3, where the A sites are statistically occupied by the M-ions. Our ESR results on powdered samples of $La_x WO_3$, doped with Gd can be summarized as follows [15]:

1. No Korringa relaxation rate occurs.

2. A distorted Dysonian line shape, which is due to nonresolved crystal field splitting is observable.

3. The linewidth of the ESR transition as function of the Gd-concentration is broadened by dipolar interactions.

4. No magnetic ordering occurs up to 15 % Gd and to 3.5 K [16], and no exchange narrowing of the ESR lines takes place.

Figure 7 shows the linewidth of the ESR-transition as function of Gd-concentration for two x-values. The measured linewidths fit the expected curve, which is calculated under the assumption of pure dipole interaction between the Gd-ions.
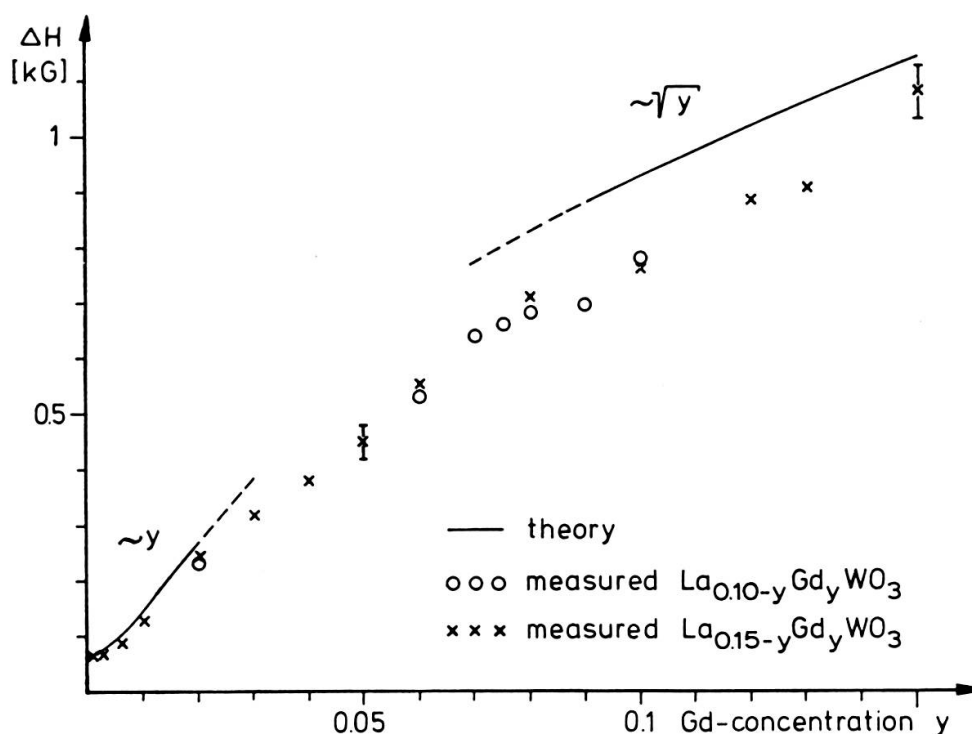

FIG. 7. — ESR on metallic $La_{x-y}Gd_y WO_3$ bronces; linewidth as function of the Gd concentration y.

III. EXCHANGE NARROWING EFFECTS
IN SOME Eu- AND Gd COMPOUNDS

In the second part of this report exchange narrowing effects in the ESR spectra of some RE compounds of the type $RE^{2+}X^{2-}$ (which should be insulating) and $RE^{3+}X^{2-}$ (which should show metallic behaviour) are discussed. Here we have

to confine ourself to one question to the problem of interaction of localized $4f$-moments with the charge carriers. Figure 8 shows a review of properties of some of these compounds.

$$RE^{2+} X^{2-} \longleftrightarrow RE^{3+} X^{2-}$$

<u>Na Cl - structure</u>

Eu	S	ferromagnetic	(T_c=16.5 K), semicond.
Gd	S	antiferromagn.	(T_N= 60 K), metallic
Y_{1-x} Gd$_x$	S		metallic

<u>Cs Cl - structure</u>

Eu	B$_6$	ferromagnetic	(T_c = 9K), semicond.
Gd	B$_6$	antiferromagn.	(T_N= 16K), metallic
La$_{1-x}$ Gd$_x$	B$_6$		metallic

FIG. 8. — Review of electric properties of *EuS*, *GdS*, *EuB$_6$* and *GdB$_6$*

We examined *EuS*, *GdS* and the diamagnetically diluted metallic compound $Y_{1-x}Gd_xS$. All these systems crystallize in the *NaCl* structure.

EuB$_6$ and *GdB$_6$* crystallize in the *CsCl*-structure, where *RE* ions and B_6 octahedra occupy the lattice sites. But they have magnetic properties very similar to the mentioned sulphides. *EuB$_6$* is a degenerate ferromagnet with $T_c \approx 9 K$, where *GdB$_6$* is like *GdS* an antiferromagnetic metallic compound with $T_N \sim 16 K$.

What do we expect in the *ESR* spectra of these concentrated *RE* compounds in the paramagnetic region?

Besides the Zeeman-term the Hamiltonian contains crystal field, hyperfine field, dipol field and exchange interactions. We can estimate, that the dipole interaction dominates within the broadening mechanisms. An isotropic exchange interaction between the *RE* ions is responsible for a line narrowing.

The fundamental process of exchange narrowing of dipolar contributions is discussed in reference [17] and [18] within the theory of linear response. It turns out, that the observed spectrum $I(v)$ is the Fournier transformation of the magnetization correlation function and depends immediately on the correlation function of the local fields.

The exchange narrowed *ESR* linewidth behaves analogous to the examples of motional narrowing. The expected features of exchange narrowing of dipolar interactions may be summarized in a schematic plot, which is shown in figure 9. We find the expected linewidth as a function of a reciprocal effective exchange field H_e. This exchange frequency in magnetic field units is direct proportional to the exchange parameters between the localized moments. But the proportional factor depends on the special form of the correlation functions.

On the reciprocal axis of figure 9 we find two magnetic field marks, the reciprocal resonance field H_z, which is calculated by the Zeeman term of the
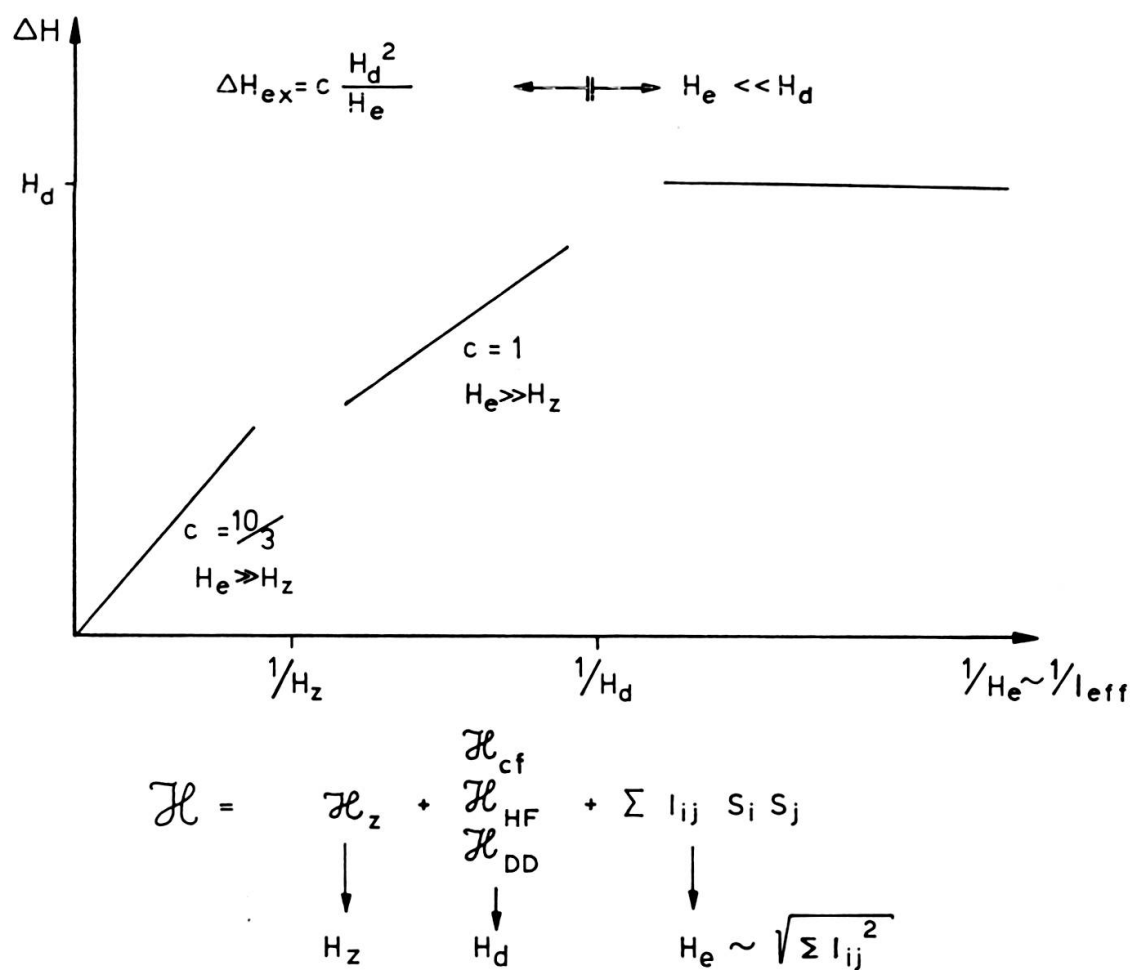
FIG. 9. — Exchange narrowing of a dipolar broadened *ESR* line; effective exchange field H_e; second moment of the broadening mechanism H_d; resonance frequency H_z.

Hamiltonian, and H_d, the square root of the second moment of the broadening mechanism, the dipole interaction. In the region $H_d < H_d$ no line narrowing is expected, the lineshape is Gaussian and the linewidth should be determined by dipole

interaction. The range $H_e \gg H_d$ is the range of line narrowing. For these simple cubic systems, the width of the narrowed Lorentzian line is given by

$$\Delta H_{ex} = \frac{c\, H_d^2}{H_e} \tag{1}$$

where

$$c = 1 \text{ if } H_e \ll H_z$$

$$c = \frac{10}{3} \text{ if } H_e \gg H_z$$

As known, the additional contribution to the exchange narrowed linewidth, in the case $H_e \gg H_z$, occurs by modulation not only of the diagonal parts of the dipole interaction but also of the nondiagonal parts.

Till now we assumed, that the effective relaxation rate in magnetic field units can be neglected compared with ΔH_{ex}. The validity of this relation is limited by considering the homogeneous linewidth of the transition ΔH_{hom}. Furthermore, we do not want to take into consideration effects of critical fluctuations near the magnetic phase transitions.
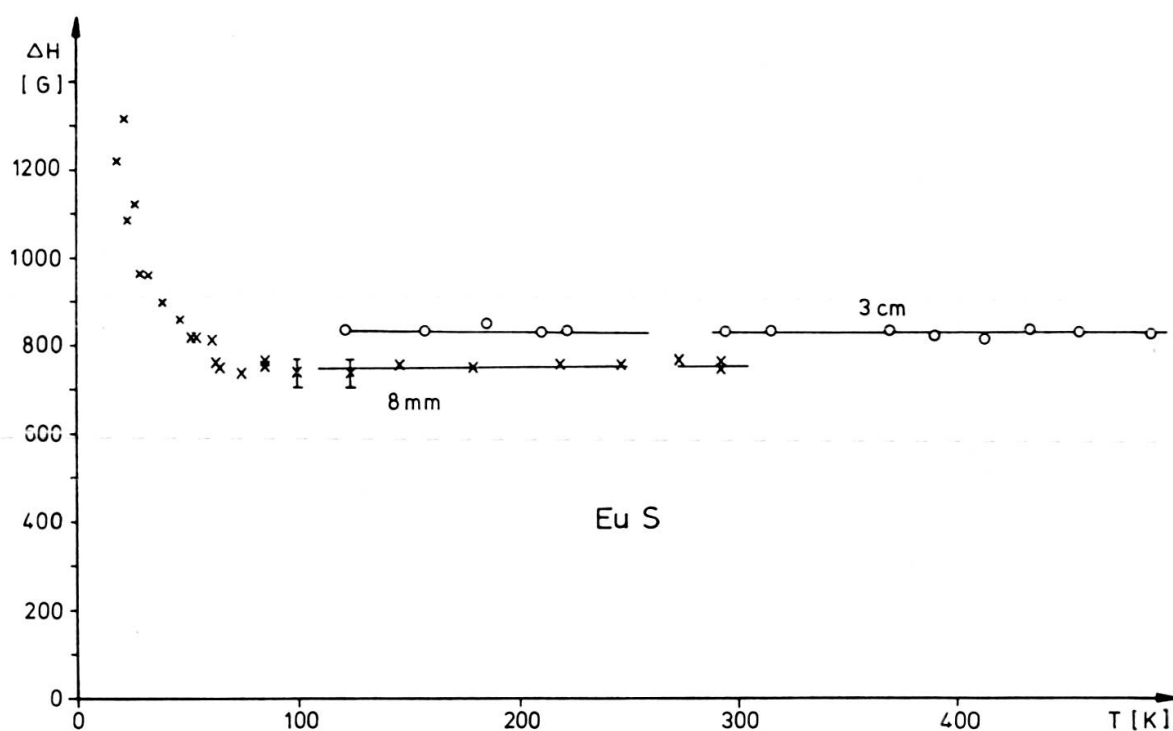

FIG. 10. — *ESR* on *EuS* powder sample; temperature dependence of the linewidth at two resonance frequencies.

Figures 10-13 show some results of the temperature dependence of the *ESR*-linewidth for the concentrated samples.

A symmetric Lorentzian line is observed for *EuS* above the ordering temperature. The linewidth above the range of critical spin fluctuations is essentially temperature independent. It amounts to 830 *G* in the 3 *cm* band and about 750 *G* in the
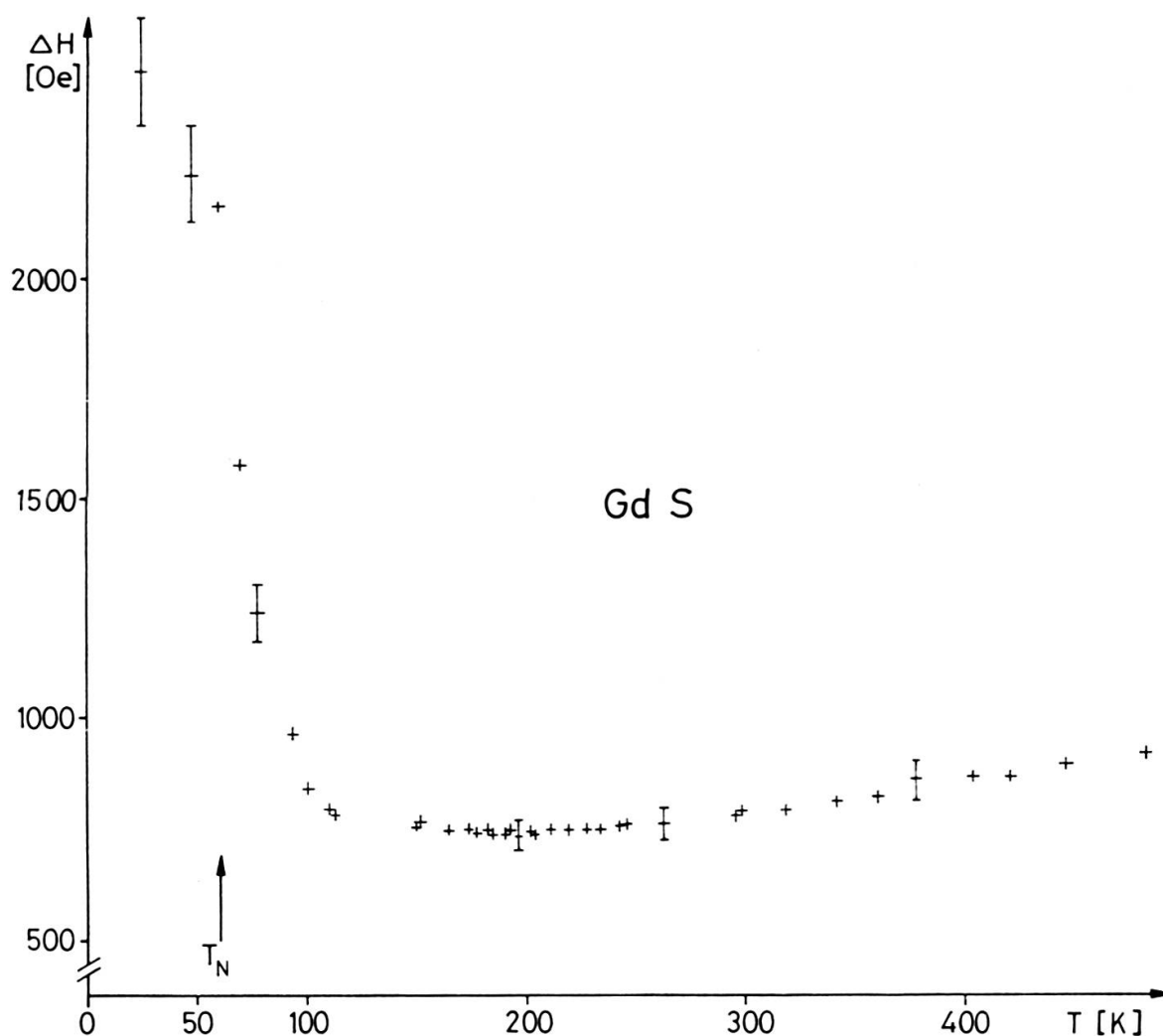

FIG. 11. — *ESR* on *GdS* powder sample; temperature dependence of the absorption part of the linewidth; no frequency effect is observable.

8 *mm* band, a slight frequency effect is observable, but no temperature variation.

The metallic *GdS*, however, has a Dysonian lineshape. The temperature dependence of the linewidth is similar to that of *EuS*. But at higher temperatures we observe

the linewidth increasing with a slope of about $0.8 \, \dfrac{G.}{K}$

Figures 12 and 13 show the *ESR* linewidth for the degenerate semiconductor EuB_6 and the metallic compound GdB_6. In both cases Dysonian *ESR* lines were observed.

For EuB_6 the high temperature linewidth is remarkably frequency dependent. At room temperature it amounts to 770 *G* in the 3 *cm* band, to 710 *G* in the 1.2 *cm*

band and to 650 *G* in the 8 *mm* band. Furthermore we observe a decreasing linewidth with increasing temperature. Within the errors of measurements the linewidth decreases by $0.3 \dfrac{G}{K}$.
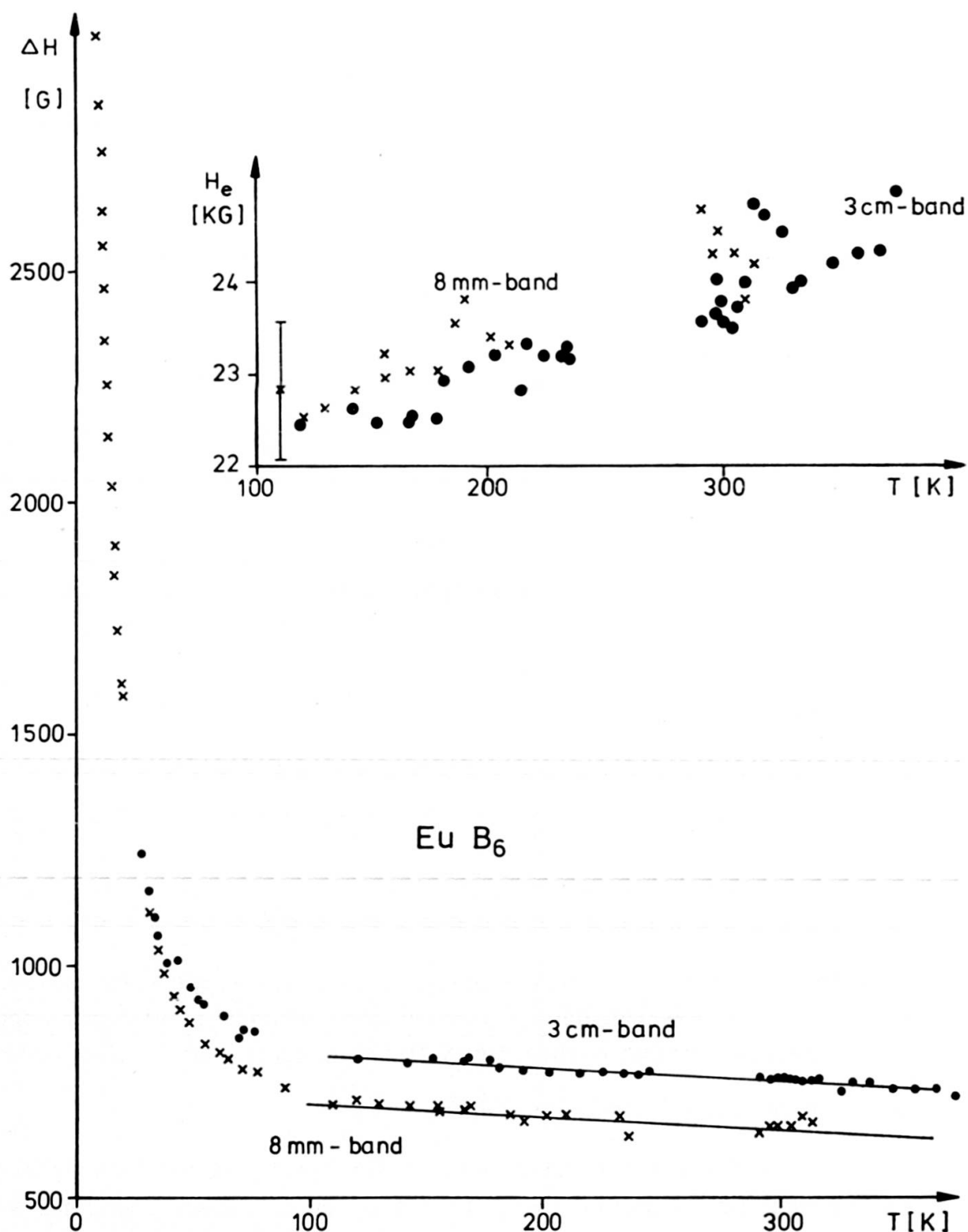

FIG. 12. — *ESR* on *EuB$_6$* powder sample; temperature dependence of the absorption part of the linewidth of two resonance frequencies. The inset shows the effective exchange frequency in magnetic field units H_e as function of temperature.

Altogether, the metallic GdB_6 shows a similar temperature behavior of ΔH like GdS. Its room temperature value amounts to about only 280 G. The slope of the increasing high temperatures linewidth is about $0.6 \dfrac{G}{K}$, a value as in GdS.
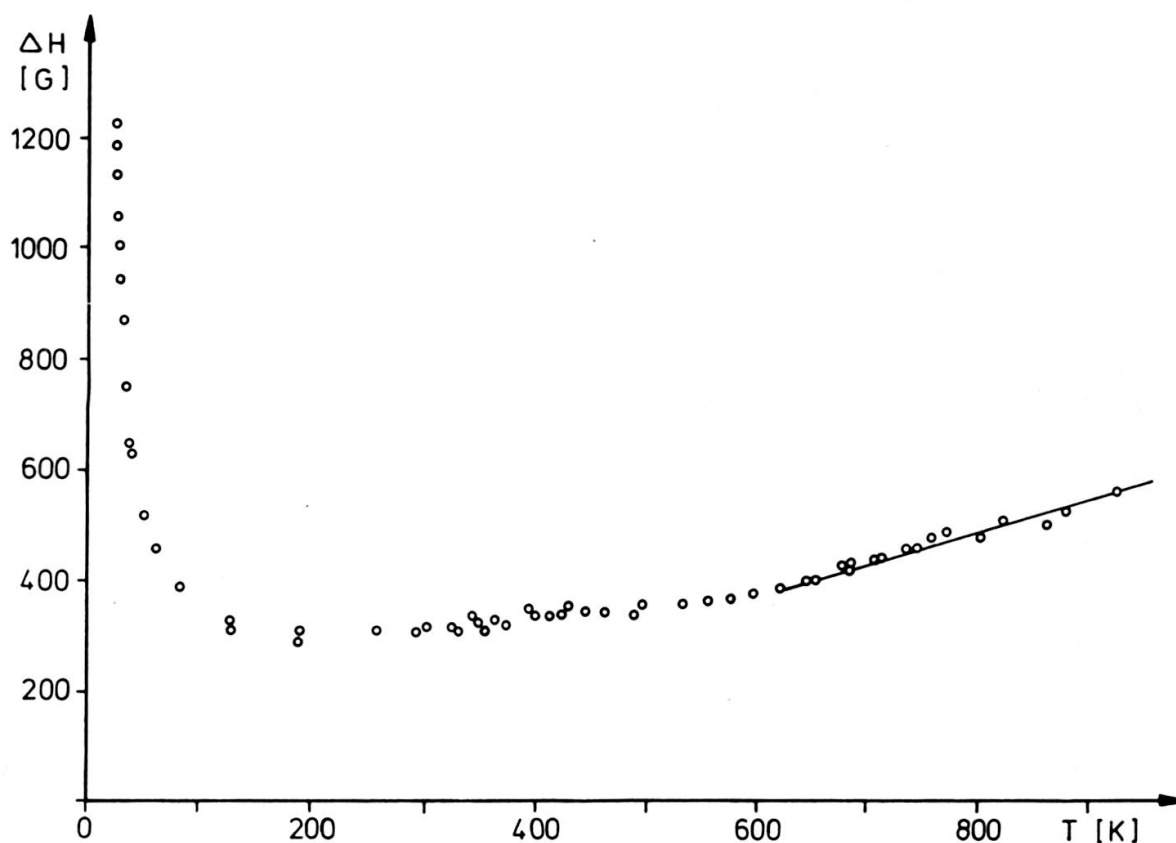

FIG. 13. — ESR on metallic GdB_6 powder sample; temperature dependence of the linewidth.

How do these results correlate with known or assumed interaction mechanisms of $4f$-ions in these compounds? Let us first discuss EuS and EuB_6.

The dominant contribution of the broadening mechanisms is due to dipolar interaction, the shape of this ERS line should be Gaussian and its width should amount to about $(2-3)\,kG$ for EuS and EuB_6. The observed linewidth in the range above the critical spin fluctuations is essentially smaller and turns out to be determined by exchange narrowing.

From the relation (1) we can get a estimate for H_e, if ΔH_{ex} is measured and the second moment H_d^2 is calculated. For EuS and EuB_6 the exchange field H_e turns out to be about $45\,kG$ for EuS and $24\,kG$ for EuB_6.

Let us first discuss the frequency effects and then the temperature variation of the exchange narrowed ESR line.

If we write $c = 1 + \dfrac{7}{3}f$ we have the relation $\Delta H_{ex} = \left(1 + \dfrac{7}{3}f\right) \cdot \dfrac{H_d^2}{H_e}$ with $f = 0$ and $f = 1$ in the two limiting cases of (1). Figure 14 shows the behavior of the parameter f as a function of the quotient (H_e/H_z) with the two values 0 and 1. We calculated this curve using the often assumed Gaussian function for the time dependence of the random field.
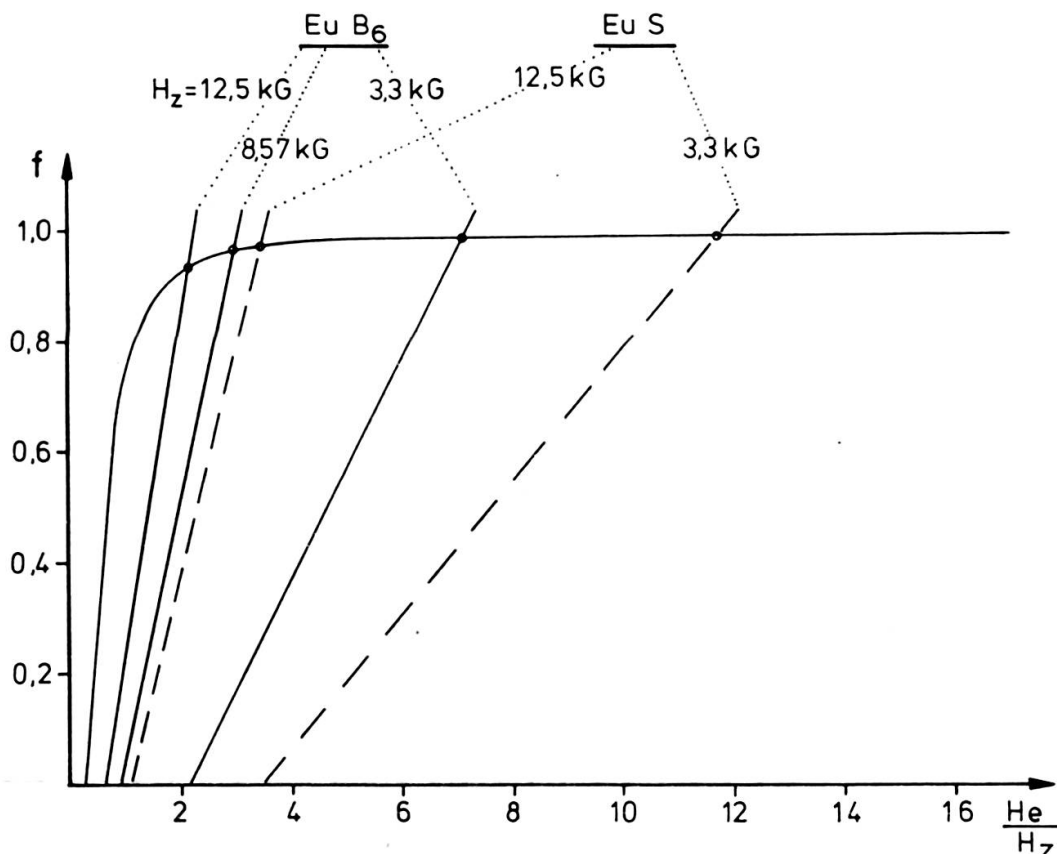

FIG. 14. — $\Delta H_{ex} = \left(1 + \dfrac{1}{3}f\right) \cdot \dfrac{H_d^2}{H_e}$; factor as function of the ratio H_e/H_z.

Equation (1) leads to a linear relation for the parameter f as a function of (H_e/H_z). The straight lines for the measured linewidths ΔH_{ex} for three different resonance fields in the 3 cm-, 1.2 cm- and 8 mm band are also shown in figure 14 for EuB_6. Their interceptions with the curve f as a function of (H_e/H_z) determine the expected f values.

The parameter f decreases between the 3 cm- and 8 mm band by a value which should be observable for EuB_6. The observed frequency dependence of ΔH_{ex} for EuB_6, therefore, is caused by the fact that H_e is only about twice as large as the resonance field $H_z \approx 12\ kG$ at 35 GHz. The relation $H_e \gg H_z$ is not fulfilled.

Figure 14 also demonstrates the situation for *EuS*, the exchange field amounts to about 45 *kG*. The variation of *f* is smaller than in the case of EuB_6 due to the larger value of H_e, in agreement with the experiment.

The frequency effect in EuB_6 and *EuS* can clearly be attributed to the modulation of the nonsecular dipolar contributions. This experimental evidence is a sure proof that we have observed an exchange narrowed linewidth and that we may apply relation (1) to EuB_6 and *EuS*.

This exchange frequency in magnetic field units H_e is directly connected with the exchange parameters between the localized moments. Assuming the isotropic Hamiltonian the following relation holds:

$$H_e \sim \sqrt{\sum I_{ij}^{\;2}}.$$

The numerical proportional factor can be calculated for a special shape of the correlation function of the variing fields. We do not want to discuss in this paper the systematic deviation between calculated and measured values of H_e, because of the limited validity of the chosen Gaussian correlation functions.

The temperature independence of the exchange narrowed linewidth ΔH_{ex} is understandable in the case of *EuS* because these parameters should be essentially temperature independent.

Contrary to *EuS*, the exchange narrowed *ESR* linewidth of EuB_6 decreases with increasing temperature and we interpret this effect as being due to an increasing value of H_e.

Little is known about the exchange mechanism in such degenerate semiconducting systems. Let us discuss some possible contributions to the exchange mechanism:

Direct or superexchange should cause an essentially temperature independent exchange field H_e, or—due to lattice expansion—a slightly decreasing value. An indirect interaction by scattering of valence electrons (Bloembergen-Rowland-mechanism) also leads to temperature independent exchange parameters.

Nondegenerate conduction electrons always yield a ferromagnetic interaction between the localized moments but the value of the exchange parameters diminishes at higher temperatures. In a degenerate conduction electron gas, indirect interaction by scattering of conduction electrons is temperature independent, if the number of charge carriers remains constant.

The metallic GdB_6 has one conduction electron per *Gd* site. For EuB_6 this value is dependent on the sample preparation, but usually is below 5-10% of the GdB_6 charge carrier concentration. Halleffect measurements [19] show an increase in the number of charge carriers between 30 *K* and 300 *K*.

We, therefore, interpret the temperature decrease of the exchange narrowed *ESR* linewidth as due to an increase in the strength of the exchange field H_e. H_e as function of temperature is shown in the inset of figure 12. This effect may be caused by the temperature dependent charge carrier concentration.

Besides our temperature dependent exchange narrowed *ESR* linewidth there are further arguments, which support the assumption that EuB_6 is a ferromagnetic semiconductor with significant interaction between *Eu*-moments and charge carriers [19]:

a) Below a temperature of 80 *K*, a deviation from the Curie-Weiss law is observable, the effective *Eu-Eu* exchange parameters are temperature dependent.

b) Measurements of electrical resistivity near the ordering temperature show evidence of a Fisher-Langer type anomaly.

The occurence of an exchange interaction between localized moments and charge carriers is more clearly visible in the *ESR* spectra of the *GdS* and GdB_6 samples. We remember, that above the temperature of critical spin fluctuations a nearly temperature independent linewidth occurs, and we observe at higher temperatures the linewidth ΔH broadening with a slope of about 0.8 G/K with increasing temperature.

Assuming that the 4*f*-4*f* exchange parameters of these metallic compounds are temperature independent, our results can only be interpreted under the assumption that the observed exchange narrowed linewidth $\Delta H(T)$ is not determined by the relation H_d^2/H_e but by the homogeneous linewidth ΔH_{hom} (line broadening mechanisms).

We have estimated the linewidth $\Delta H_{ex} = c \dfrac{H_d^2}{H_e}$ using known exchange parameters in the molecular field approximation. For *GdS* we get a value of $\Delta H_{ex} \sim 400\ G$, essentially smaller than the observed linewidth of $\Delta H \sim 800\ G$. For $\Delta H_{\text{hom}} \gg \Delta H_{ex}$, the narrowing process of the dipolar broadening takes place only till the homogeneous linewidth ΔH_{hom} is reached. This effect is similar to the broadening of the motional narrowed *ESR* line of *d*-electrons in the $Na_x V_2 O_5$ compounds at higher temperatures.

Such linearly increasing *ESR* linewidths are observable in some concentrated metallic alloys like *GdAg* [20], $GdAl_2$ [21], etc. Their often discussed slope amounts to $(1-5)\dfrac{G}{K}$. The increasing linewidth is usually interpreted as being due to relaxation by *s-f* exchange interaction and corresponding bottleneck effects.

The best way to prove the occurence of exchange interaction between localized 4*f* moments and conduction electrons in *GdS* and GdB_6 is to study *ESR* spectra of correspondingly diluted samples. Therefore, let us briefly mention our results of *ESR* on $Y_{1-x}Gd_xS$ [23].

At low *Gd* concentrations Dysonian *ESR* lines are observable at low temperatures. The absorption part has Lorentzian character. The linewidth ΔH as function of temperature T is found in figure 15 for $Y_{1-x}Gd_xS$ for several *Gd* concentrations.

The linewidth increases with temperature. The slope $\dfrac{\Delta H}{T}$ increases with decreasing Gd concentration and amounts to about $12\,\dfrac{G}{K}$ in the isothermal case. Parallel to the increasing slope we observe a measurable g-shift. It reaches an isothermal value of $+\,0.018$.
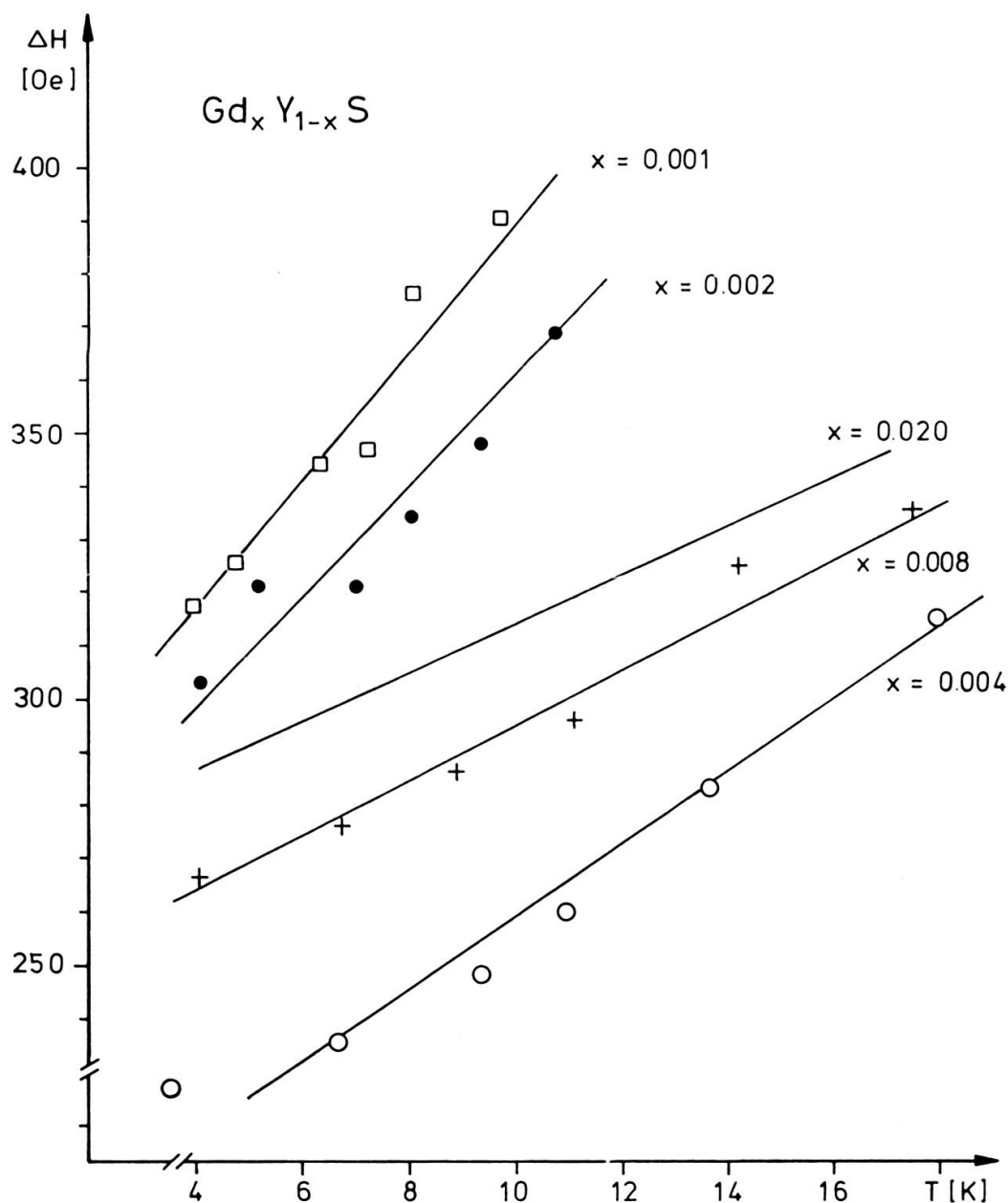

FIG. 15. — *ESR* on $Gd_x Y_{1-x}S$ powder samples; linewidth as function of temperature; $\nu \approx 35\ GHz$.

We got a similar behavior of the linewidth in the metallic compound $La_{1-x}Gd_xB_6$, too.

We interpret these results in the usual way [22] as evidence for:

1. interaction of localized moments with charge carriers in these compounds—which are often called semiconductors—like in metallic alloys. A reasonable density of state leads to an *s-f* interaction parameter of about 0.1 *eV*,

2. The occurrence of at least partial *s*-character of the conduction electrons because bottleneck effects are taking place.

IV FINAL COMMENTS

The experimentally observed features of motional and exchange narrowing in the here discussed transition element compounds may be summarized as follows:

If contributions of the homogeneous linewidth may be neglected the hyperfine or dipole broadened linewidth narrows until the relation

$$\Delta H \sim \frac{v^2 \text{ broad}}{v_e(T)}$$

is reached. We discussed the possibility to get—from this relation—an estimate for the hopping or exchange frequency $v_e(T)$.

In the case of the mentioned nonstoichiometric vanadium- or molybdenum compounds we could correlate the temperature dependent hopping frequency with the mobile character of the *d*-electron. In the case of the semiconducting *Eu* compounds we may correlate this frequency with the exchange parameters.

If the homogeneous linewidth ΔH_{hom} is larger than ΔH_{ex} the narrowed linewidth is determined by these processes which shorten the effective lifetime of the localized moments.

The effective relaxation rate was determined by excitation to a conduction band in the case of the nonstoichiometric V_2O_5 and MoO_3 compounds and by exchange interaction with conduction electrons in the metallic *Gd* compounds.

REFERENCES

[1]   S. METHFESSEL, D. C. MATTIS, Handbuch der Physik XVIII/1, p. 389, 1968, Springer-Verlag Berlin.

[2]   J. P. SUCHET, Crystal Chemistry and Semiconduction in Transition Metal Binary Compounds, Academic Press N.Y. (1971).

[3]   D. S. VOLZHENSKII, M. V. PASHKOVSKII, Soviet Phhysics — Solid State *11*, 950, (1969).

[4]   J. H. PERLSTEIN, J. Solid State Chemistry *3*, 217, (1971).

[5]   P. NAGELS, M. DENAYER, Procceedings 10th Int. Conf. Physics of Semiconductors 1970, p. 321.

[6]   V. A. JOFFE, I. B. PATRINA, Soviet Physics—Solid State *10*, 639 (1968).

[7]   V. A. JOFFE, I. B. PATRINA, Phys. Status Solidi *40*, 389 (1970).

[8]   G. SPERLICH, Z. Physik *250*, 335 (1972).

[9]   P. W. ANDERSON, Phys. Rev. *109*, 1492 (1958).

[10] P. W. ANDERSON, J. Phys. Soc. Japan *9*, 316 (1954).

[11] P. ZIMMERMANN, Phys. Rev., *B8*, 3917 (1973).

[12] H. A. EICK, L. KIHLBORG, Acta Chemica Scandinavica *20*, 1658 (1966).

[13] G. BANG, G. SPERLICH, to be published.

[14] W. H. JONES, E. A. GARBATY, R. G. BARNES, J. Chem. Phys. *36*, 494 (1962).

[15] G. SPERLICH, K. JANSEN, G. BANG, Phys. Letters, *45A*, 423 (1973).

[16] W. OSTERTAG, Inorganic Chemistry *5*, 758 (1966).

[17] P. W. ANDERSON, P. R. WEISS, Rev. Mod. Phys. *25*, 269 (1953).

[18] R. KUBO, K. TOMITA, J. Phys. Soc. Japan *9*, 888 (1954).

[19] R. BACHMANN, K. N. LEE, T. H. GEBALIE, J. Appl. Physics *41*, 1431 (1970).

[20] E. BURZO, I. URZU, J. PIERRE, Phys. Stat. Sol. b *51*, 463 (1972).

[21] D. DAVIDOV, D. SHALTIEL, Phys. Rev. *169*, 329 (1968).

[22] D. DAVIDOV, A. CHELKOWSKI, C. RETTORI, R. ORBACH, M. P. MAPLE, Phys. Rev. B *7*, 1029 (1973).

[23] P. URBAN, G. SPERLICH, Solid State Communications *14*, 591 (1974).