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# EXCHANGE AND CRYSTAL FIELD PARAMETERS FROM TESR OF $Al:Er$ \*

BY

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Transmission Electron Spin Resonance (*TESR*) has principally been applied to the study of the conduction spin resonance of pure metals, alloys with nonmagnetic impurities, and alloys containing magnetic impurities which show the bottleneck phenomenon. We would like to show, using the system of  $Al:Er$  (5-35 ppm) as an example, that the unbottlenecked *TESR* of the conduction electrons combined with the normal reflection *ESR* of the rare earth ions can yield useful information about the crystal field splittings of the rare earth *f*-shell, the magnitude and *k*-dependence of the conduction electron-rare earth ion exchange coupling, and the enhancement of the host crystal susceptibility.

Because of the high reactivity and low solid solubility of rare earth impurities in aluminum, reliable samples could not be prepared using conventional techniques. Instead a "getter-sputtering" technique was used. It involved first sputtering clean the surfaces of a high purity aluminum foil of appropriate thickness ( $\sim 0.05$  mm) for the *TESR* experiments, sputtering on a thin layer of rare earth impurities, diffusing these impurities into the foil by annealing just below the melting temperature of the foil, and then rapidly quenching the alloy to room temperature. All of these operations are carried out in situ, where reactive gas partial pressures are kept to a negligible level by the gettering action of the rare earth metal which is being continuously sputtered on to the cold walls of the main deposition chamber. Relative concentrations are determined by residual resistivity measurements and compared with absolute concentration determinations from neutron activation analysis. Consistent scaling of neutron activation analysis, *TESR* results, and resistivity measurements indicate that the samples are metallurgically satisfactory.

Figures 1 and 2 give the experimental results for the resonance shift and line-widths of the *TESR* relative to the values for pure aluminium. The dramatic decrease in resonance field as the temperature is lowered can be attributed to the exchange

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interaction of the conduction electrons with the temperature dependent magnetization of the rare earth ions, the converse of the Knight shift. There is also a very large impurity contribution to the linewidth which is interpreted as the sum of spin-flip scattering via spin orbit interaction in the outer electron shells of the rare earth ions (a process assumed independent of the presence of the local moment on the

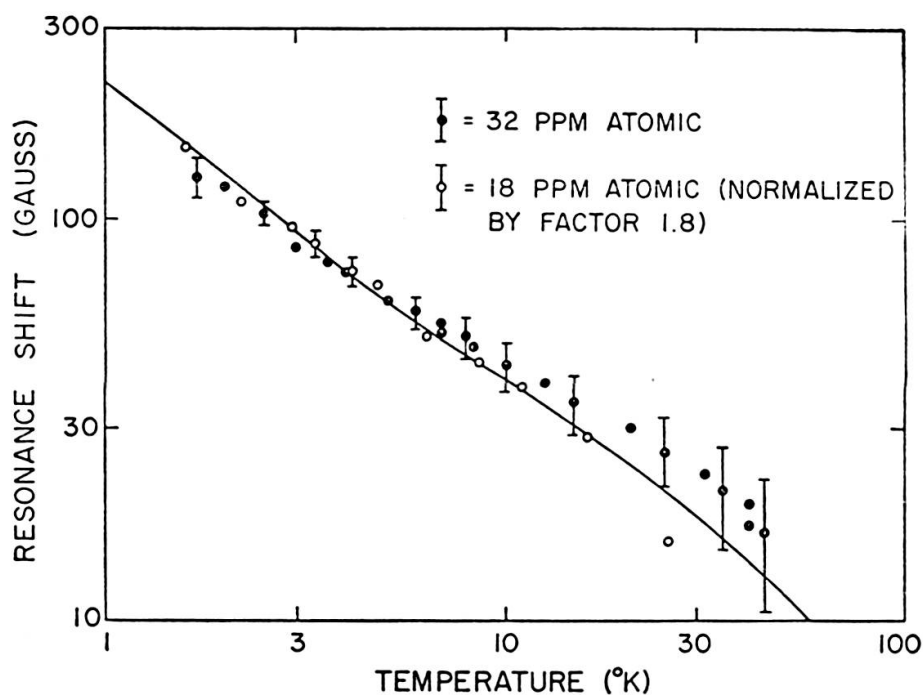


FIG. 1. — Shift (in gauss) of the  $Al:Er$  TESR data relative to pure aluminium, for an erbium concentration of 32 ppm and for 18 ppm appropriately scaled, as a function of temperature.

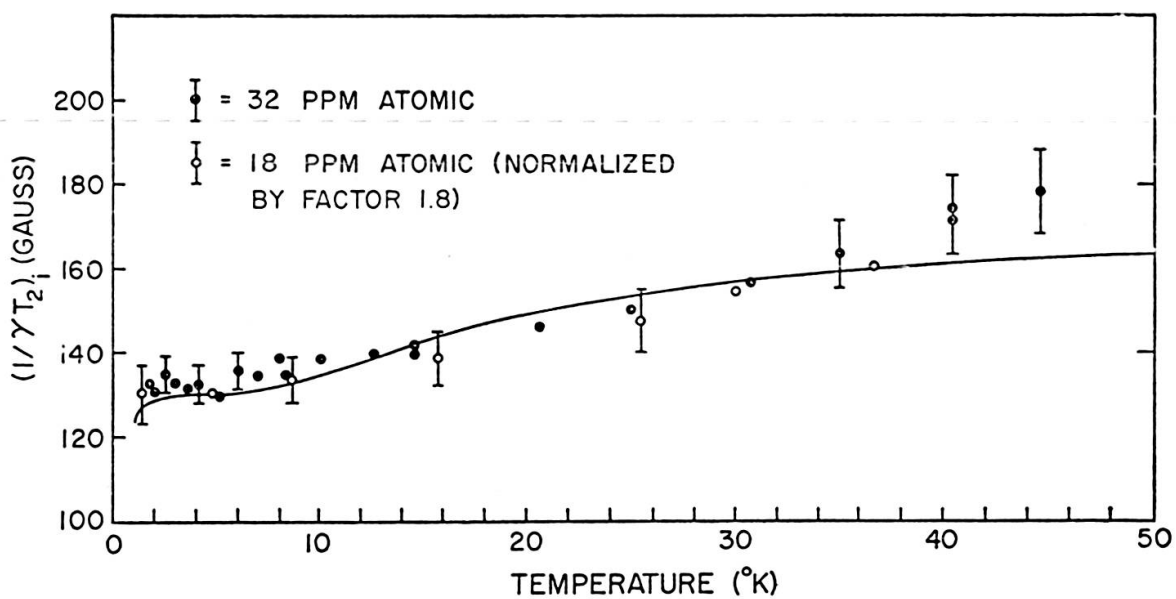


FIG. 2. — Excess line width, over pure aluminium, of the  $Al:Er$  TESR as a function of temperature.

impurity), plus an exchange scattering from the local moment. This latter process is temperature dependent since the magnetic moment and therefore the exchange scattering depends sensitively upon the thermal populations of the various crystal field levels of the rare earth ions.

In addition to the results illustrated in these figures, the results of the normal *ESR* measurements of the rare earth resonance near  $g = 6.8$  give some additional information. In particular, one measures both the  $g$ -shift relative to the free ion value, or Knight shift, of the rare earth resonance and the temperature dependence of the linewidth, or Korringa broadening. If we assume that the exchange interaction has the simple form  $-\vec{J}\vec{S}\cdot s$ , where  $J$  is the exchange constant, we obtain the  $g$ -shifts and widths of the two resonance signals:

$$\begin{aligned}\delta g_f &\sim J\rho \\ \delta g_s &\sim c_f J\chi_f(W, x, T) \\ \Delta H_f &\sim \{(J\rho)^2 kT + \text{background}\} \\ \Delta H_s &\sim c_f \{J^2\rho G(W, x, T) + \text{spin orbit scattering}\}\end{aligned}$$

$\rho$  is the density of states at the Fermi surface, and  $c_f$  the concentration of the rare earth impurities.  $\chi_f(W, x, T)$  is the magnetic polarizability for the rare earth ions, which depends upon the conventional crystal field parameters  $W$  and  $x$ .  $G$  is similarly a function, conveniently defined to approach 1 as  $T \rightarrow 0$ , which describes the temperature dependence of the exchange scattering. Note that it is this temperature dependence which in fact allows the separation of the temperature independent spin orbit mechanism from the exchange scattering mechanism.

The lines in the figures give the theoretical fit to the temperature dependence obtained with the parameters  $W = 0.6$  and  $x = -0.3$ , corresponding to a  $\Gamma_7 - \Gamma_8(^1)$  splitting, the most important parameter in fitting the data, of  $45^\circ K$ . At high temperatures the experimental data deviate significantly from the theoretical curves. However, the high temperature data is suspect because at these temperatures the relaxation rates are becoming fast enough that dynamical or bottlenecking effects may well be influencing the measured shifts and linewidths. Therefore, from the temperature dependence of the *TESR* shift and broadening induced by the presence of the rare earth ions, we obtain the crystal field splitting of the ions. Note that the technique is applicable as well to ions whose ground states are non-magnetic as long as there are magnetic low lying crystal field levels which can be thermally populated. Furthermore, it is not necessary to be able to observe the rare earth resonance in order to extract these parameters. Indeed, we have studied thulium, which has a singlet and hence non-magnetic ground state, and again we observe an easily measureable temperature dependent broadening and shift of the *TESR* line.

In addition to determining the crystal field parameters, the fits to the four relations above give four independent measures of the exchange parameter  $J$ , and these are found to differ significantly from one another. There are two (at least)

reasons for these discrepancies which relate to the oversimplification of the problem implied by the simple  $s$ - $f$  exchange model. First, because of the finite extent of the  $4f$  shell, the exchange interaction with the conduction electrons may not be considered as a point interaction and the exchange constant  $J$  should be thought of as depending upon the wave vectors of the incident and scattered conduction electrons. The shifts  $\delta g_s$  and  $\delta g_f$  depend upon  $\langle J(k, k) \rangle_{E_F}$  while the broadening terms,  $\Delta H_s$  and  $\Delta H_f$  depend upon  $\langle |J(k, k')|^2 \rangle_{E_F}$ . The importance of this distinction is clear from our results which give an experimentally deduced  $\langle J(k, k) \rangle_{E_F}$  30% larger than  $\langle |J(k, k')|^2 \rangle_{E_F}^{\frac{1}{2}}$ . Second, the measured parameters  $\delta g_f$  and  $\Delta H_f$ , through their dependence upon the host magnetic susceptibility, are influenced by host susceptibility enhancement factors not included in the simple expressions above, and again differently for the  $\delta g_f$  and  $\Delta H_f$ , while these enhancement factors do not influence the parameters  $\delta g_s$  and  $\Delta H_s$ . (R. Orbach has pointed out that  $\Delta H_s$  also is influenced by the enhancement, changing somewhat our initial analysis. The quantitative interpretation has been submitted for publication). Therefore, these four determinations of  $J$  yield information about both the  $k$ -dependence of  $J$  and the host susceptibility enhancement factors. In fact, a preliminary data analysis suggests that the susceptibility enhancement in aluminium is significantly smaller than has been predicted by calculations based on a free electron model. However, we await a completion of the data analysis, and in particular of the error analysis, before drawing more specific conclusions concerning the quantitative results.

In summary, these experiments on the system of  $Al:Er$  have demonstrated the feasibility of the *TESR* technique to determine both rare earth crystal field splittings and some of the details of the rare earth-conduction electron exchange coupling, and in particular to demonstrate the anticipated inadequacy of the simplest exchange model which assumes a constant value of  $J(k, k')$ .