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ANOMALOUS ESR BEHAVIOUR OF SOME RARE-EARTH INTERMETALLIC COMPOUNDS ABOVE THE NEEL POINT

BY

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ABSTRACT

The intermetallic compounds GdB_6, GdB_4, $GdZn_{12}$ and Gd_2Zn_{17} show line broadening in their *ESR* spectra at 8,3 · 5,5 and 10 times respectively their antiferromagnetic ordering temperature (T_N). In addition they show deviations from Curie Weiss Law behaviour well above T_N and $|\theta|/T_N = 1$. Much smaller deviations are observed for the *Tb* or *Dy* analogs of these compounds and here $|\theta|/T_N \sim 1$. The compounds Ag_3Gd, Cu_2Gd and Al_2Eu are however well-behaved, ΔH broadening at less than $2T_N$; $EuAl_4$ and Cu_4Gd appear to show intermediate behaviour. The above effects in the anomalous compounds are tentatively attributed to an extensive regime of short range order above T_N.

The *ESR* behaviour of a number of intermetallic compounds containing *Gd* ($4f^7$) and divalent *Eu* ($4f^7$), which order antiferromagnetically at low temperatures has been studied at *X*-band using powder samples.

The *ESR* behaviour of the metallic Rare-earth borides GdB_6 and GdB_4 is shown in figures 1 and 2. The most notable feature of the data in both compounds is that line broadening sets in at about $8T_N$ in the case of GdB_6 ($T_N = 13\,K$) and $3.5T_N$ for GdB_4 ($T_N = 42\,K$). The resonant frequency shows no sign of a shift until much lower temperatures and, indeed, the shift which occurs could be easily accounted for by a small overestimate of the lineshape correction factor for such broad lines.

Whilst the *ESR* linewidth in these compounds shows the most striking effects, there are also anomalies in the static susceptibility and electrical resistivity above the Néel point. In GdB_6, there are pronounced deviations from Curie Weiss Law behaviour at about 90 *K* (Coles and Griffiths, 1961) and in GdB_4 the electrical resistivity shows anomalous behaviour between 14 *K* and 80 *K*, where the resistance is lower than the curve expected in the absence of ordering. (Fisk *et al.*, 1971). As may be seen from Table 1, in both GdB_6 and GdB_4, $|\theta|/T_N \gg 1$ whilst in the compounds DyB_6 and DyB_4 $|\theta|/T_N \sim 1$ and no significant deviations are observed in, for example, the resistivity of DyB_4 (Fisk *et al.*, 1971). The anomalous behaviour thus appears to be greatest in the *S*-state ion *Gd* ($4f^7$).

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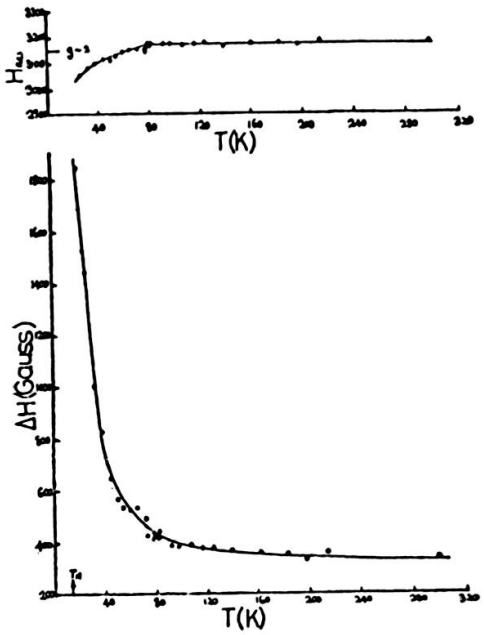

FIG. 1. — Temperature dependence of the *ESR* resonant frequency and linewidth of GdB_6. Correction has been made in this and subsequent figures for lineshape and finite sweep speed.

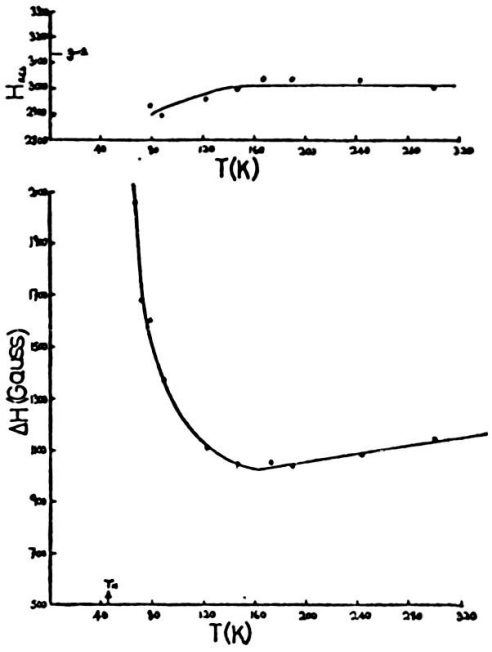

FIG. 2. — Temperature dependence of the *ESR* resonant frequency and linewidth of GdB_4.

We have also investigated the *ESR* behaviour of a number of other compounds which order antiferromagnetically at low temperatures—namely $GdZn_{12}$, Gd_2Zn_{17}, $GdCu_4$, $GdCu_2$, $GdAg_3$, $EuAl_2$ and $EuAl_4$—in order to see if these compounds show similar *ESR* behaviour to the *Gd* borides above their Néel temperatures.

Compound	gpm.	T_N K	$\lvert\theta\rvert/T_N$	$\lvert\theta\rvert$ / T_N·Dy,Tb	Tg* K	T ΔH K	ΔH Room Temp. GAUSS	$\frac{d\Delta H}{dT}$ GK^{-1}
GdB_6	2.00±0.01	14	4	1 (Dy)	~60	~100	334±15	-
GdB_4	2.10±0.03	42	1.5	1(Dy)	-	~130	1143±55	-
Ag_3Gd	2.00±0.02	33	~0.3	-	~60	~70	1200±60	0.7±0.2
$EuAl_2$	2.002 ± 0.005	15	~0	-	~30	~30	953±45	1.2±0.3
$EuAl_4$	2.000± 0.005	15	-	-	~40	~40	550±20	0.3±0.1
Cu_2Gd	2.013± 0.005	41	-	-	~60	~65	1200±60	2.5±0.2
"Cu_4Gd"	2.01± 0.01	18	-	-	~40	~50	-	4.5±1.5
$Zn_{12}Gd$	1.980± 0.005	16	3.6	2.7(Tb)	~30	~75	250±12	0.25±0.1
$Zn_{17}Gd_2$	1.995± 0.005	10	5.3	0.6(Tb)	~15	~95	308±15	0.3±0.1

† $\lvert\theta\rvert/T_n$ for Dy or Tb compounds of same crystal structure

* Tg, TΔH - temperatures at which a resonant lineshift and broadening first set in.

TABLE 1 Summary of magnetic data for compounds

Figure 3 shows the *ESR* results for the compound Cu_2Gd ($T_N = 40\,K$). The compound Ag_3Gd ($T_N = 35\,K$) shows similar behaviour. In both these cases the *ESR* line begins to broaden at only 1.5-2T_N and in both cases the resonant field moves away strongly from the temperature independent paramagnetic *g*-value at about the same temperature as line broadening first sets in. The compound $EuAl_2$ shows very similar behaviour. Very few magnetic data exist for these compounds but in both Ag_3Gd and $EuAl_2$ (table 1) the ratio $|\theta|/T_N$ is small and susceptibility measurements on the compound Ag_3Gd suggest that there are no deviations from linearity in a plot of $1/\chi$ *vT* until close to T_N.

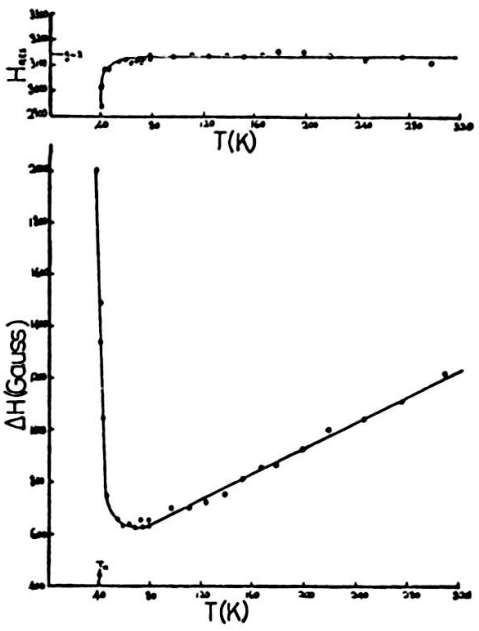

FIG. 3. — Temperature dependence of the *ESR* resonant frequency and linewidth of Cu^2Gd.

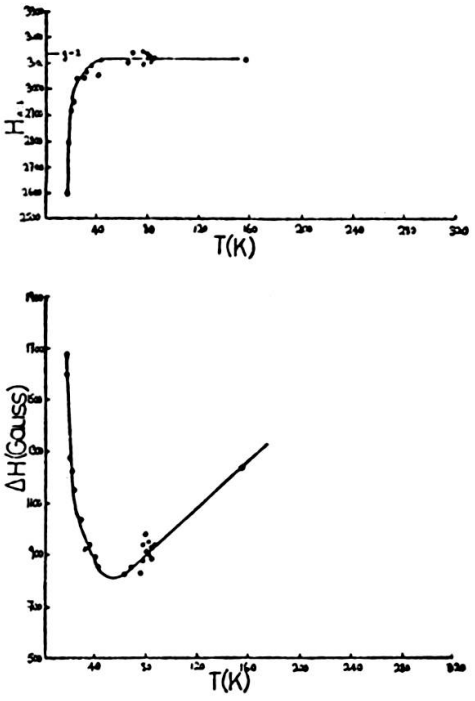

FIG. 4. — Temperature dependence of the *ESR* resonant frequency and linewidth of Cu_4Gd.

We have also measured a compound which forms close to stoichiometry Cu_4Gd, the structure of which is unknown. Resistivity measurements, however, suggest that it orders into an antiferromagnetic configuration below 18 *K*. The *ESR* results are shown in figure 4 and it is clear that the *ESR* behaviour is intermediate between that of the anomalous compounds and those which are well-behaved. In this case line broadening sets in at about 50 *K* (2.7T_N). The compound $EuAl_4$ shows similar behaviour, broadening at about 2.6T_N.

Stewart (1971, 1973) has studied in detail the magnetic properties of the compounds $GdZn_{12}$ and Gd_2Zn_{17}. The former orders antiferromagnetically at

16 K and has a Curie Weiss θ of $-58\,K$, showing strong deviations from linearity in a plot of $^1/\chi$ vT at about 50 K. Similarly the compound Gd_2Zn_{17} orders at 10 K, $\theta/T_N = -5.3$ and, again, shows strong deviations from linearity in $^1/\chi$ vT (at about $4T_N$). For both compounds (particularly Gd_2Zn_{17}) the value of $^{|\theta|}/T_N$ is reduced in the Tb compounds. The ESR behaviour is shown in figures 5 and 6 and it is apparent that the form of the data is similar to that of the borides. In the case of Gd_2Zn_{17}, for example, the linewidth broadens at $10T_N$ but we note that no shift in the resonant frequency becomes apparent until about $1.5T_N$, where again, the linewidth is sufficiently broad to make accurate corrections to the resonant field for lineshape extremely difficult.

These results thus show that the anomalous magnetic behaviour above T_N first observed in GdB_6 and GdB_4 is not unique. The Zn-Gd compounds show the same type of behaviour and the compounds "Cu_4Gd" and $EuAl_4$ appear to be intermediate in behaviour between the anomalous compounds and those such as Cu_2Gd, Ag_3Gd and $EuAl_2$ which are well-behaved. An ESR study of a number of Gd and Eu compounds which order ferromagnetically at low temperatures (Taylor and Coles, to be published) does not show anomalous behaviour.

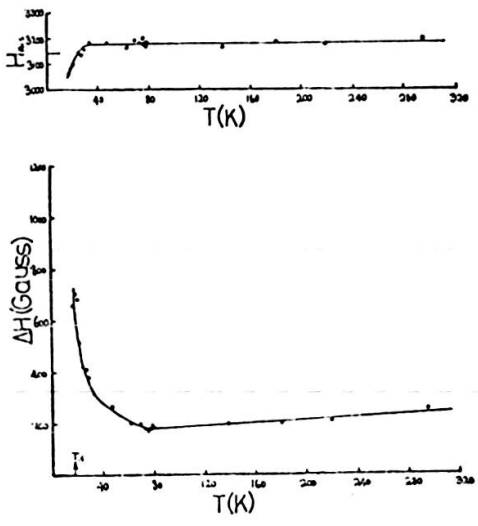

FIG. 5. — Temperature dependence of the ESR resonant frequency and linewidth of $GdZn_{12}$.

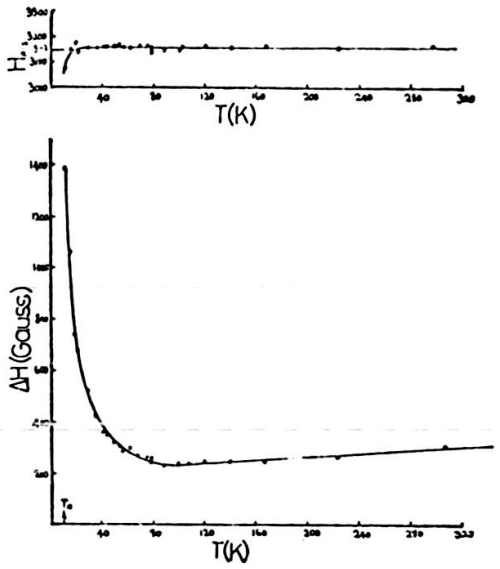

FIG. 6. — Temperature dependence of the ESR resonant frequency and linewidth of Gd_2Zn_{17}.

Crystal field effects in compounds containing $Gd\,(4f^7)$ and $Eu\,(4f^7)$ are expected to give rise to splitting no greater than 1 K (Fisk (1969) has showed that Gd in YB_6 follows a Curie Weiss Law down to at least 1.5 K). In our previous paper (Fisk *et al.*, 1971), we proposed two possible mechanisms for the observed behaviour.

The first was that the formation of superzone band gaps at a temperature $\sim 1\theta 1$ may prevent magnetic ordering at this temperature from going to completion. The compound then orders into an alternative spin structure at lower temperatures. The second explanation, which we now tend to favour, bearing in mind the observations reported here of anomalies in compounds of widely different band structures, is that there exists in these materials an extensive regime of short range magnetic order above the Néel point. Why this should be greater for some compounds than in others and why it appears to predominate in *S*-state ions, is not yet clear. We note that in *MnO*, short range magnetic order is observed in neutron scattering at room temperature (Shull *et al.*, 1951) although the Néel point is 116 *K*; furthermore $^{1\theta 1}/T_N = 5.3$ and *ESR* studies have shown line broadening at about $3.5T_N$. (Battles, 1971). It has very recently been reported (Moon, 1973) that Gd_2O_3, which orders antiferromagnetically at 1.6 *K* shows short range magnetic order at 300 *K*.

Full analysis of this problem is, at present, hindered by the shortage of available magnetic studies. Neutron diffraction studies of the compounds might directly determine the extent of any short range order and an attempt could be made to correlate the presence of anomalies with magnetic structures, which in all but one case ($TbCu_2$) are unknown. Unfortunately the common isotope of *Gd* has a high neutron absorption cross-section and measurements have to be made on the *Tb* compounds. Preliminary results on samples of TbB_6 and TbB_4, prepared from the separated B_{11} isotope, show strong magnetic peaks at 4.2 *K*.

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