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MAGNETIC STRUCTURE AND PROPERTIES OF EQUIATOMIC RARE EARTH GERMANIDES

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Summary

Magnetic measurements were made on the compounds EuGe, DyGe and TmGe. The first two compounds order antiferromagnetically at 20 K and 37 K respectively. For TmGe antiferromagnetic ordering is observed below 4.2 K. The magnetic structure of orthorhombic DyGe was investigated by neutron diffraction and shown to be antiferromagnetic with propagation vector $\boldsymbol{k} = [00\frac{1}{2}]$. The magnetic properties of all RGe compounds (R ≡ rare earth metal) are reviewed. It is shown that the magnetic coupling constant changes from positive to negative as the RGe series is passed through.

1. Introduction

Members of the series of isostructural rare earth intermetallic compounds generally show uniform magnetic properties in the sense that they are all ferromagnetic or all antiferromagnetic. The reason for this is that the scheme for the interaction between the magnetic moments remains the same throughout the whole series. An important variable is the size of the spin moment of the rare earth atoms, with the consequence that the strength of the magnetic interaction varies smoothly through the series, having a maximum in the middle of the series. However, there are several exceptions to this general behaviour. One of these exceptions is the series of equiatomic rare earth germanides in which the ordering temperature seems to vary in a somewhat haphazard manner [1]. In several neutron diffraction studies we have investigated the magnetic structures formed in these compounds [2 - 5]. It follows from these studies that also their magnetic structure is far from uniform. A wealth of different structure types is displayed, ranging from simple ferromagnetism and antiferromagnetism to various types of incommensurate structures.

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In the present study we will present some supplementary experimental information on the magnetic properties of several RGe compounds (R ≡ rare earth metal). We will review the magnetic properties of all RGe compounds and show that at least part of their anomalous behaviour arises as a consequence of a non-uniform magnetic coupling mechanism in this series.

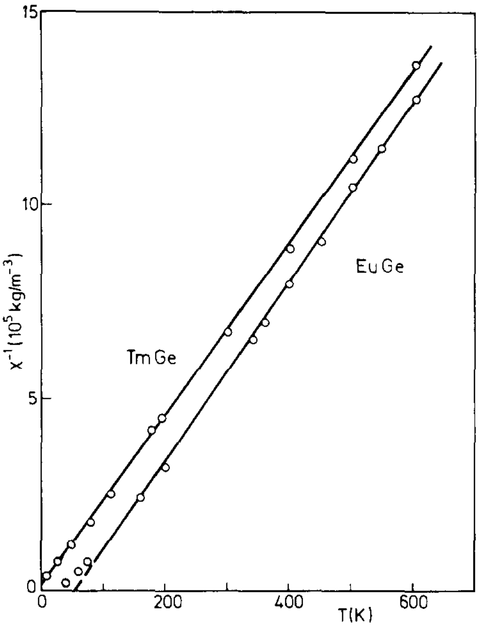
2. Experimental procedure and results

The samples of EuGe, DyGe, TmGe and CeGe studied in the course of the present investigation were prepared by means of arc melting in an atmosphere of purified argon gas. The purity of the starting materials was 99.9% for the rare earth elements and 99.99% for germanium. X-ray diffraction showed that all samples have the orthorhombic CrB-type or FeB-type structure. Magnetic measurements were made in the temperature range 4.2 - 600 K using an adaptation of the Faraday method.

Neutron diffraction measurements were made on DyGe in the paramagnetic state (70 K) and in the magnetically ordered state (9 K). The neutron data were collected with the double-axis multi-counter system at the Saphir reactor in Würenlingen using a wavelength of $\lambda = 2.352$ Å. The step increment of the diffraction angle 2θ was 0.20°. In view of the high absorption cross-section of the sample ($\sigma_{Dy} = 580$ b for $\lambda = 1.08$ Å [6]), we used an annular vanadium sample holder of thickness 0.5 mm and outer diameter 7.5 mm [7]. A computer program written by M. Schärli and based on ref. 7 was used. In this experimental arrangement the count rate of the strongest nuclear reflection (111) was equal to 30 counts $\min^{-1}$. The data were corrected for absorption with a special program and evaluated by the Rietveld profile analysis method for all nuclear and magnetic structures [8].

Preliminary neutron diffraction data obtained on CeGe and TmGe indicate that the former compound does not show long-range order at temperatures down to 1.2 K whereas for the latter a few magnetic lines were observed below 4.2 K. These peaks correspond to reciprocal lattice positions $k \neq 0$ and thus suggest antiferromagnetic order. However, the indexing of magnetic satellites at 1.2 K has not yet been possible on the basis of simple multiples of the C cell. Further experiments are under way.

Results of magnetic measurements made on the compounds EuGe and TmGe are shown in Fig. 1. The results obtained on DyGe are basically the same as those obtained earlier [1]. At high temperatures all compounds display Curie–Weiss behaviour, as may be seen also from the data in Fig. 1. The effective magnetic moments derived from the slope of the temperature dependence of the reciprocal susceptibility (χ^{-1}) are equal to 7.79 μ_B per europium atom for EuGe and 7.44 μ_B per thulium atom for TmGe. These values are close to the free ion μ_{eff} values for Eu^{2+} (7.94 μ_B), Dy^{3+} (10.63 μ_B) and Tm^{3+} (7.57 μ_B) respectively. Whereas TmGe shows Curie–Weiss behaviour down to 4.2 K, deviations from linear χ^{-1} *vs.* T behaviour occur for EuGe and DyGe at temperatures well below 100 K. For DyGe these



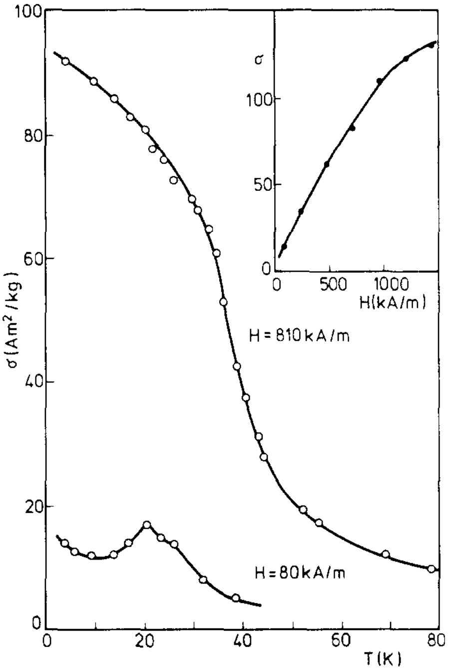


Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility in EuGe and TmGe.

Fig. 2. Temperature dependence of the magnetization of EuGe at two different field strengths. The inset shows the field dependence of the magnetization at 4.2 K.

deviations are associated with the occurrence of a Néel-type transition at $T_N = 37$ K. Results of magnetic measurements made on EuGe in the low temperature region are shown in more detail in Fig. 2. In low magnetic fields the temperature dependence of magnetization $\sigma(T)$ shows a cusp-like behaviour commonly encountered in magnetic transitions of the Néel type. However, in high external fields the $\sigma(T)$ curve has a shape reminiscent of a paramagnetic-to-ferromagnetic transition. These results indicate that EuGe may be characterized as metamagnetic.

No spin flip transition is evident in the $\sigma(H)$ curve (shown for $T = 4.2$ K in the inset of Fig. 2) very probably because our measurements were made on polycrystalline material. Nevertheless, it follows from the results shown in the inset of Fig. 2 that in the ultimate field strength considered by us ($H = 1440$ kA m^{-1}) the σ value observed corresponds to 5.5 μ_B, which in turn corresponds to about 80% ferromagnetic alignment of the Eu^{2+} moments.

Results of the neutron diffraction measurements are shown for DyGe in Figs. 3 and 4. The data of Fig. 3 pertain to the paramagnetic state so that the neutron diagram is composed of nuclear reflections only. The nuclear parameters obtained after refinement of the data are listed in the first column of Table 1.

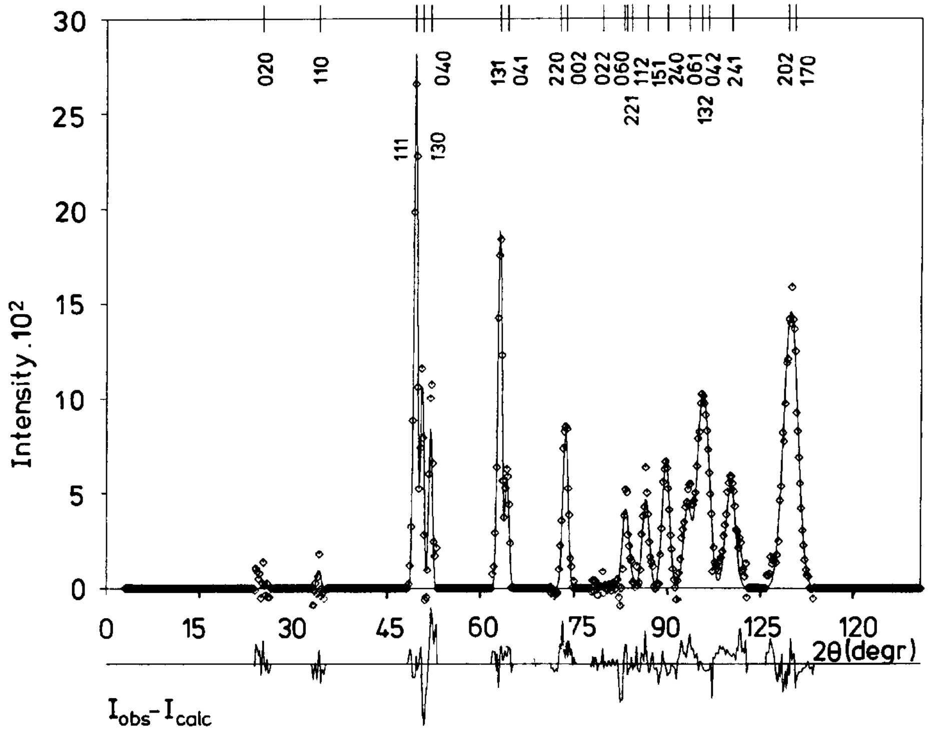


Fig. 3. Neutron diffraction pattern of DyGe in the paramagnetic state at 70 K. The full curve through the experimental data points represents the calculated profile. The difference diagram is indicated at the bottom of the figure.

TABLE 1

Refined structural and magnetic parameters from the neutron data of DyGe, corresponding to space group *Cmcm*, sites 4(c), $\mp(0y\frac{1}{4})$

Parameter	*70 K*	*9 K*
a (Å)	4.254(1)	4.254(1)
b (Å)	10.623(2)	10.617(2)
c (Å)	3.904(1)	7.793(2)
y_{Dy}	0.1385(4)	0.1369(5)
y_{Ge}	0.4227(7)	0.4235(9)
μ_z (μ_{B})	—	9.0(1)
$R_{\mathrm{n}}^{\mathrm{I}}$	6%	8.3%
$R_{\mathrm{m}}^{\mathrm{I}}$	—	8.6%
R_{wp}	12.5%	15.2%
R_{exp}	10.6%	9.5%

μ_z is the ordered moment of dysprosium parallel to the c-axis.

$R_{\mathrm{n}}^{\mathrm{I}}$, $R_{\mathrm{m}}^{\mathrm{I}}$ and R_{wp} are the reliability factors for the observed and calculated nuclear integrated, magnetic integrated and weighted profile intensities.

R_{exp} is the expected value related to the statistical accuracy of the data.

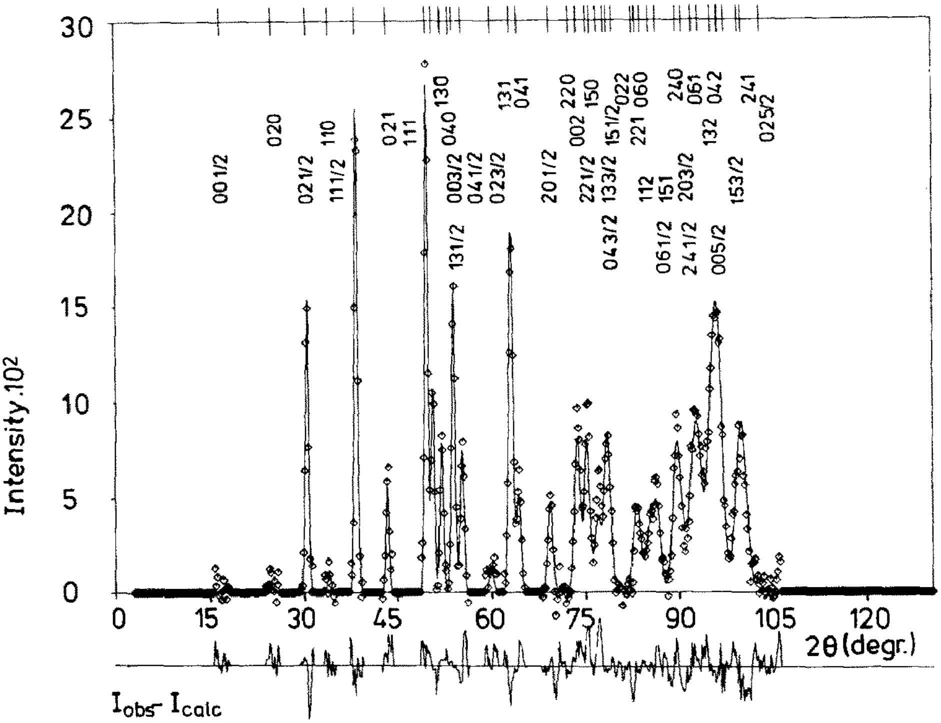


Fig. 4. Neutron diffraction pattern of DyGe in the magnetically ordered state at 9 K. The full curve through the experimental data points represents the calculated profile. The difference diagram is indicated at the bottom of the figure.

However, the neutron diffraction pattern at 9 K given in Fig. 4 shows clearly the appearance of magnetic peaks associated with long-range magnetic ordering. The indexing of these magnetic lines indicates that the magnetic unit cell is twice as large as the chemical unit cell when viewed in the c direction, the corresponding propagation vector of the magnetic structure being $k = [00\frac{1}{2}]$.

From the observation that magnetic reflections $00l$ with $l = 2n + 1$ are absent it follows that the magnetic moment direction is parallel to the c direction. The magnetic space group is C_c2/c (Sh^{90}_{15}) similar to that of TbGe [3]. Neutron diffraction measurements showed this type of antiferromagnetic ordering in DyGe to be stable down to 1.5 K. The ordered magnetic moment of dysprosium at saturation (9.0 ± 0.1 μ_B) is found to fall below the free ion value ($gJ = 10$ μ_B for Dy^{3+}), which is presumably due to crystal field effects. The neutron data obtained at 9 K were used for a complete structure determination. Observed and calculated integrated neutron intensities can be compared in Table 2, and the corresponding refined parameters are listed in the second column of Table 1. Schematic representations of the nuclear and magnetic structures are shown in Fig. 5.

TABLE 2

Observed and calculated integrated neutron intensities of DyGe at 9 K corresponding to a uniaxial antiferromagnetic structure (the indexing (*hkl*) refers to the chemical cell)

h	*k*	*l*	2θ (deg)	I_{nuc}	I_{mag}	I_{tot}	I_{obs}	*ESD*[a]
0	0	1/2	16.83	—	0	0	302	168
0	2	0	25.07	92	—	92	519	159
0	2	1/2	30.56	—	1830	5261	4797	167
0	−2	1/2	30.56	—	3371			
1	1	0	34.11	347	—	347	390	153
−1	1	1/2	38.47	—	8242	8289	8150	177
1	−1	1/2	38.47	—	47			
0	2	1	43.44	1822	—	1822	2537	153
1	1	1	49.63	8864	—	8864	9427	162
1	3	0	50.68	3741	—	3741	3562	122
0	4	0	52.07	2786	—	2786	3038	144
0	0	3/2	53.30	—	0	0	0	0
1	3	1/2	53.95	—	288	5766	5776	157
1	−3	1/2	53.95	—	5473			
0	4	1/2	55.28	—	2205	2816	3015	143
0	−4	1/2	55.28	—	611			
0	2	3/2	60.00	—	359	554	1071	160
0	−2	3/2	60.00	—	195			
1	3	1	63.09	8289	—	8289	7879	168
0	4	1	64.30	2280	—	2280	2645	151
2	0	1/2	69.38	—	2357	2357	2025	195
2	2	0	72.56	66	—	66	0	
0	0	2	73.72	4506	—	4506	5124	160
2	2	1/2	75.26	—	1597	4593	5385	150
2	−2	1/2	75.26	—	2942			
1	5	0	75.94	7	—	7	7	0
1	3	3/2	76.96	—	2166	2280	3113	123
1	−3	3/2	76.96	—	114			
0	4	3/2	78.07	—	252	1163	1245	41
0	−4	3/2	78.07	—	911			
1	5	1/2	78.61	—	3873	4477	4433	151
1	5	1/2	78.61	—	604			
0	2	2	79.49	69	—	69	0	110
0	6	0	82.77	2	—	2	—	7
2	2	1	83.22	3068	—	3078	2546	181
1	1	2	84.07	436	—	436	448	31
0	6	1/2	85.39	—	239	2219	2229	109
0	−6	1/2	85.89	—	1980			
1	5	1	86.50	3174	—	3174	3600	151
2	4	0	89.67	5953	—	5953	5629	176

[a] Estimated standard deviation.

The temperature dependence of the magnetic $11\frac{1}{2}$ reflection is shown in Fig. 6. From these data the magnetic ordering temperature $T_N = 37 \pm 1$ K was derived. This value agrees with the ordering temperature obtained from magnetic measurements.

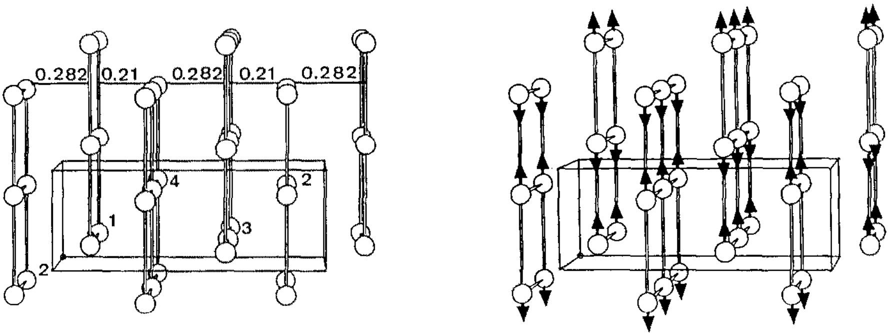


Fig. 5. Schematic representations of the nuclear (left) and magnetic (right) structures for DyGe (only Dy are shown).

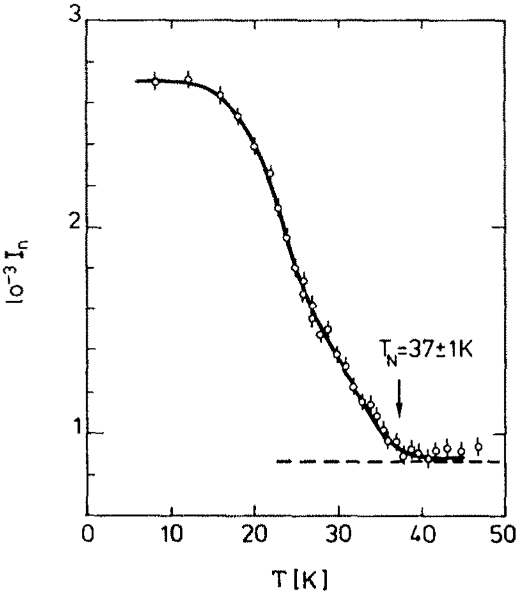


Fig. 6. Temperature dependence of the intensity of the magnetic reflection $11\frac{1}{2}$ in the neutron diffraction pattern of DyGe.

3. Discussion

The data obtained from magnetic measurements and neutron diffraction for various members of the series RGe are compared in Table 3. The second and third columns list values of the effective moment μ_{eff} and the asymptotic Curie temperature θ_p derived from magnetic measurements. The fourth column gives values of the magnetic ordering temperature which may be either the Curie temperature T_C or the Néel temperature T_N. For compounds with R ≡ Ce, Sm, Eu and Gd the ordering temperatures listed correspond to bulk magnetic measurements; in all other cases the values

TABLE 3

Survey of magnetic properties of RGe compounds as derived from bulk magnetic measurements and neutron diffraction

Compound[a]	μ_{eff} (μ_B per R atom)	θp (K)	T_{ord} (K)	*Magnetic structure*	μ_{ord} (μ_B per R atom)	*Reference*
CeGe	2.41	+10	$T = 9$	—	—	1
PrGe	3.5	+25	$T_c = 36.5$	Ferromagnetic	2.9	2
PrGe	3.69	+30	$T_c = 42$	Ferromagnetic	3.27	2
NdGe	3.69	+25	$T_c = 26$	Ferromagnetic	2.38	2
SmGe	—	—	$T = 40$	—	—	1
EuGe	7.79	+60	$T = 20$	—	—	This investigation
GdGe	8.21	−13	$T = 62$	—	—	1
TbGe	9.76	−5	$T = 60$	AF[b]; $k = [\frac{1}{2}0\frac{1}{2}]$; AF; $k = [00\frac{1}{2}]$	8.35	3
DyGe	10.60	−5	$T = 36$	AF; $k = [00\frac{1}{2}]$	9.0	This investigation
HoGe	10.77	−5	$T = 18$	AF; $k = [q_x 0 q_z]$	7.3	4
ErGe	9.70	−7	$T = 6$	AF; $k = [00q_z]$	6.87	5
TmGe	7.44	−8	$T < 4.8$	AF; unknown	—	This investigation

[a] All compounds have the orthorhombic CrB structure except CeGe which is of the FeB type [9]. The compound PrGe is polymorphic (*c.f.* FeB and CrB).

[b] AF, antiferromagnetic.

listed were derived from neutron diffraction experiments. The fifth column gives a survey of the magnetic structures revealed by neutron diffraction; the corresponding moments (at 4.2 K) are listed in the last column of the table.

The interesting aspect in the class of RGe compounds is the large variety in magnetic structures observed on passing through this series. It may be seen from the table that ferromagnetism prevails at the beginning of the series while antiferromagnetism is found in the compounds with heavy rare earth metals. Two magnetic structures occur in TbGe [3]. In the range $29\ \mathrm{K} \leqslant T \leqslant 60\ \mathrm{K}$ the magnetic structure is similar to that described in the preceding section for DyGe. At $T_t = 29$ K there is a first-order phase transition to a different antiferromagnetic structure which has a propagation vector $k = [\frac{1}{2}0\frac{1}{2}]$ and is stable at lower temperatures. The compound HoGe displays even more exotic behaviour [4]. Its magnetic structure is incommensurate with the crystal lattice in two directions. Both wave vector components vary with temperature [10] and reach a value close to $k = [\frac{1}{2}0\frac{1}{2}]$ at the lowest temperature considered. The antiferromagnetic structure of ErGe is incommensurate with the crystal lattice in the c direction [5].

It is difficult to trace the origin of the occurrence of such a complicated sequence in magnetic structures. Most probably this is the result of competing ferromagnetic and antiferromagnetic interactions between the various types of R-neighbour atoms. Some insight into the magnetic coupling between the R moments may be obtained by closer inspection of the values of the asymptotic Curie temperatures. These values are a measure of the sign and magnitude of the average exchange interaction between the R spins. According to the molecular field approximation the following equation is given

$$\theta_p = \text{constant} \times J_{ex}(S_i \cdot S_j) = \text{constant} \times J_{ex}(g-1)^2 J(J+1) \qquad (1)$$

If the spin–spin coupling were the same throughout the RGe series the exchange constant J_{ex} would not vary with R, meaning that θ_p would be proportional to the de Gennes factor $G = (g-1)^2 J(J+1)$. Such behaviour is frequently observed in the series of rare earth compounds owing to the fact that the spin–spin coupling proceeds by means of s conduction electron polarization. In this case the constant J_{ex} is of the form $J_{ex} \propto J_{sf}^2 \Sigma_i F(2k_F R_i)$, where J_{sf} is the s–f exchange constant, k_F the Fermi wave vector and where the summation over $F(x)$ (equal to $(x \cos x - \sin x)/x$) extends over all rare earth atoms of the lattice (see for instance ref. 11). The constancy of J_{ex} then derives from the fact that $\Sigma_i F(2k_F R_i)$ shows hardly any variation through a series of isostructural compounds. Furthermore, J_{ex} can be positive or negative. This depends on the underlying crystal structure and on the magnitude of k_F.

Apart from this so-called RKKY-type interaction [12 - 14], magnetic coupling of the rare earth spins may proceed by means of the 5d electrons [15]. These electrons are accommodated in a narrow band. A certain amount of spin polarization may occur, each 4f moment polarizing its own

5d electrons. The magnetic interaction proceeding via the 5d electrons is always ferromagnetic ($J_{ex} > 0$ in eqn. (1)) and depends considerably on the interatomic separation.

It will be clear that θ_p is proportional to $(g - 1)^2 J(J + 1)$ if only one of these two types of interactions contributes to J_{ex}, or if their relative contributions do not vary within a given series of compounds.

Information on the variation of J_{ex} within a series may be obtained from the experimental θ_p data after dividing these by the corresponding G values. Values of θ_p/G which are proportional to J_{ex} for the various RGe compounds investigated have been plotted in Fig. 7. Although the experimental accuracy of the smaller θ_p values listed in Table 3 is comparatively low, this plot is quite convincing in showing that J_{ex} changes its sign around the middle of the rare earth series. In view of the sign of J_{ex} with respect to the two coupling mechanisms discussed above, the results shown in Fig. 7 suggest that a d-electron-mediated coupling mechanism prevails at the beginning of the series while the s-electron-mediated coupling predominates at the end of the series.

It is interesting to compare this variation in J_{ex} through the series with some results obtained by means of NMR investigations. In several series of rare earth intermetallics this technique was successfully used to determine the relative degree of s- and d-electron polarization operative in these compounds; the possibility of distinguishing the s- and d-electron contributions arises from the fact that their hyperfine coupling constants are of a different sign [11]. Some rules of thumb were derived from these investigations. One of these correlates the magnetic coupling between rare earth spins with the nearest-neighbour separation. For a large nearest-neighbour separation the coupling is d-electron mediated and ferromagnetic; for a small nearest-neighbour separation it is s-electron mediated and may be ferromagnetic or antiferromagnetic. The change-over point is at approximately 3.5 Å. These results may be applied to the CrB structure described in the preceding section. In this structure type the nearest-neighbour distances occur between

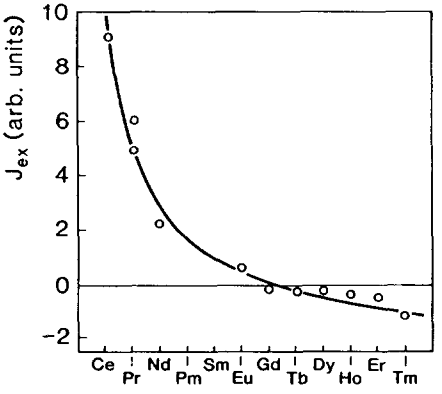


Fig. 7. Variation in J_{ex} (proportional to θ_p/G) through the series of RGe compounds ($G = (g - 1)^2 J(J + 1)$).

the atoms 1 and 2 shown in the bottom left-hand corner of Fig. 5(a). For PrGe and NdFe this distance is close to 3.7 Å and hence well inside the range of the relatively strong ferromagnetic d-electron-mediated coupling. For the end members of the RGe series this distance has dropped to 3.5 Å so that here the s-electron-mediated coupling may prevail. In other words, the behaviour of J_{ex} as shown in Fig. 7 is in accord with the predictions made in ref. 11.

To conclude, the experimental results obtained in the course of the present investigation yield a more complete picture regarding the changes in magnetic structure and asymptotic Curie temperature on passing through the series of equiatomic rare earth germanium compounds. We discussed the possibility that the different magnetic structures observed in this series are associated with the occurrence of competing types of magnetic interactions between the rare earth moments, and showed that the apparently irregular variation in the asymptotic Curie temperature over this series may be understood on the same basis.

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