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Intermetallic Compounds

R. STREET AND J. E. GOLDMAN, Chairmen

Magnetic Properties of Some Rare Earth-Aluminum Alloys

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The RAl alloys are orthorhombic; the structure can be described with a trigonal motif similar to a halfcell of CsCl. The R_4Al_2 alloys are tetragonal. The magnetic properties of the RAl alloys, where R is any rare earth from Ce to Tm, and those of the R_3Al_2 alloys, with R passing from Gd to Tm, have been measured in fields up to 25 kOe or 60 kOe and at temperatures between 1.4° and 400°K. The RAl alloys, with R from Pr to Tb, order antiferromagnetically at temperature between 20°K (PrAl) and 72°K (TbAl); the magnetic configuration of TbAl has been studied by neutron diffraction; HoAl is ferromagnetic with a Curie point at 26°K; DyAl, ErAl and TmAl exhibit metamagnetism at 4.2°K. Gd₃Al₂ is ferromagnetic with a Curie point at 282°K, close to that of Gd; Dy₃Al₂ shows an antiferromagnetic transition near 20°K in zero field and metamagnetic behavior induced by a field below this temperature; its Curie point is 76°K. All compounds exhibit a Curie–Weiss behavior above their transition points, with a paramagnetic moment close to that of the corresponding free tripositive rare earth ions.

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The rare earth-aluminum phase diagrams¹ generally present five intermetallic compounds. The magnetic properties of the $RAl_{2,2}$ RAl_{3} ³ and some RAl compounds⁴ (where R is a rare earth metal) have already been determined. We have concerned ourselves with those of the RAl and $R_{3}Al_{2}$ compounds. They are pre-

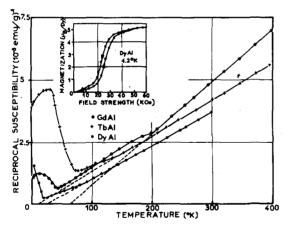


FIG. 1. Reciprocal susceptibility-temperature behavior of GdAl, TbAl, and DyAl. Magnetization-field strength behavior of DyAl at 4.2°K.

pared by melting the required proportions of the elements in a high-frequency levitation furnace. We have

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studied only compounds which were found free from all other phases by x-ray examination. The magnetizations are measured using the extraction method, in fields Hup to 25 kOe or 60 kOe and at temperatures ranging from 1.4° to 400°K.

RAI COMPOUNDS

The crystal structures of the RAl compounds belong to two types. The first type,⁵ CeAl, crystallizes in the

TABLE I. Experimental results for RAl compounds.

Compound	$\theta_{\rm C}$ (°K)	θ _N (°K)	θ_p (°K)	$M_e(\mu_{\rm B}/{ m R})$
CeAl		9	4	2.34
PrAl		20	11	3.58
NdAl		29	-4	3.53
GdAl		42	64	8.15
TbAl		72	10	10.0
DyAl		20	25	10.6
HoAl	26		17	10.7
ErAl		13	23	9.65
TmAl		10	-2	7.70

Cmcm group; LaAl and slowly cooled PrAl is isotypic with it. The second type,⁶ DyAl, crystallizes in the *Pbcm* group; the compounds from neodymium up to thulium, with the exception of europium, are isotypic with it. These structures are both formed from the same motifs: aluminum chains and trigonal prisms showing similarities with a half-cell of CsCl; only the arrangement of these motifs differs. The magnetic results obtained with CeAl and PrAl are in good agreement with those

¹K. H. J. Buschow and J. H. N. Van Vucht, Z. Metallk. 57, 162 (1966). ² H. J. Williams, J. H. Wernick, E. A. Nesbitt, and R. Sherwood,

² H. J. Williams, J. H. Wernick, E. A. Nesbitt, and R. Sherwood, J. Phys. Soc. Japan, Suppl. B-1 17, 91 (1962). ³ K. H. J. Buschow and J. F. Fast, Z. Phys. Chem. 50, 1

^{*}K. H. J. Buschow and J. F. Fast, Z. Phys. Chem. 50, 1 (1966).

⁴ F. Kissel and W. E. Wallace, J. Less-Common Metals 11, 417 (1966).

⁵ C. Bècle and R. Lemaire, Compt. Rend. **264B**, 887 (1967). ⁶ C. Bècle and R. Lemaire, Compt. Rend. **264B**, 543 (1967).

reported by Kissel and Wallace,⁴ however, the paramagnetic Curie points θ_p that we have determined are higher. NdAl, GdAl and TbAl are antiferromagnetic. DyAl exhibits a metamagnetic behavior below its order temperature (Fig. 1). HoAl has a spontaneous magnetization at low temperature, however at 4.2°K a field of 70 kOe is not sufficient to saturate it, a law of approach in 1/H gives a saturation magnetization of 6.2 $\mu_{\rm B}$ /HoAl. ErAl and TmAl are metamagnetic below the Néel temperature. At high temperature all the compounds follow a Curie-Weiss law. The effective moment M_e in Bohr magnetons, deduced from the Curie constant is in good agreement with that of the free \mathbb{R}^{3+} ion (Table I). For numerous compounds, at low temperature, the variation of the reciprocal susceptibility no longer follows a Curie-Weiss law (Fig. 1). This difference cannot be attributed to crystal field effects, since it is maximum for GdAl. But neutron diffraction studies⁷ of TbAl show at 110°K a shortrange magnetic order. Below the Néel temperature of TbAl the antiferromagnetic arrangement of the moments is not collinear; it is closely related to the existence of the trigonal prisms formed by the rare earth atoms. In fact it results from a compromise between anisotropic exchange interactions and a magnetocrystalline anisotropy exerted along two different axes.

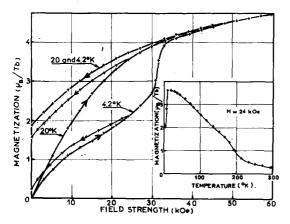


FIG. 2. Magnetization-field strength behavior at 4.2° and 20° K and temperature variation of magnetization at 24 kOe of Tb₃Al₂.

TABLE II. Experimental results for R₃Al₂ compounds.

Compound	$\theta_{\mathbf{C}}$ (°K)	$\theta_{\rm N}$ (°K)	θ_i (°K)	θ_p (°K)	$M_{\epsilon}(\mu_{\rm B}/{\rm R})$
Gd ₃ Al ₂	282			285	8.2
${ m Tb}_3{ m Al}_2$	203		11	125	9.6
Dy ₃ Al ₂	76		20	31	10.8
Ho_3Al_2	33		11	10	10.9
Er ₃ Al ₂		9		-3	9.6
Tm ₃ Al ₂		3		-10	7.8

R₃Al₂ COMPOUNDS

The R_3Al_2 compounds crystallize⁸ in the $P4_2nm$ group, their structure can be generated from rare earth chains and aluminum centered trigonal rare earth prisms. Gd₃Al₂ is ferromagnetic with a Curie temperature $\theta_{\rm C}$ at 282°K, its absolute saturation magnetization is 7.1 μ_B per gadolinium atom. Tb₃Al₂ exhibits a ferromagnetic behavior from a transition temperature $\theta_t = 10^{\circ}$ K to the Curie point (203°K), below 10°K the magnetization decreases rapidly if measured in fields lower than 30 kOe; in the higher fields, it is practically the same as it is at 20°K (Fig. 2). Dy_3Al_2 and Ho_3Al_2 have magnetic behavior similar to that of Tb₃Al₂. The temperature of the different transitions are listed in Table II. Er₃Al₂ and Tm₃Al₂ have Néel temperature at 9° and 3°K, respectively below these temperatures they are metamagnetic. At high temperature, all compounds follow a Curie-Weiss law; the effective magnetic moment of the rare earth atoms corresponds to that of the tripositive free ion. Neutrondiffraction studies of Tb₃Al₂ showed that, from 10° to 203°K, the terbium magnetic moments are parallel to one another; in a zero field, at 4.2°K, the moments are no longer collinear and exhibit a resultant which is not nil. As a conclusion, Gd₃Al₂ is typically ferromagnetic but when the rare earth spin decreases and that its orbital moment increases, the compounds exhibit an antiferromagnetic behavior more and more accentuated at low temperature and which seems due to crystal-field effects.

⁷ C. Bècle, R. Lemaire, and E. Parthé (to be published).

⁸ N. C. Baenziger and J. J. Hegenbarth, Acta Cryst. 17, 620 (1964).