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Magnetism and Phase Relations of the $PrAl_2$-$CaAl_2$, $GdAl_2$–$CaAl_2$ Systems*

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The magnetic properties and phase relations of the ternary systems $Pr_{1-x}Ca_xAl_2$ and $Gd_{1-x}Ca_xAl_2$ are reported. The first system exhibits complete miscibility whereas the second shows a miscibility gap extending from $x = 0.5$ to 0.8. The ternaries were examined magnetically to ascertain whether antiferromagnetism could be produced by replacing the trivalent rare earth ion with divalent Ca. Results for the (Pr,Ca)Al_2 system give some indication that the exchange changes sign when 80% or more of the Pr is replaced by Ca. The α-phase (Gd-rich) alloys in the (Gd,Ca)Al_2 system are ferromagnetic with Curie temperatures only modestly reduced from that of $GdAl_2$. The β-phase (Ca-rich) alloys in this system are paramagnetic to 4.2°K. The evidence suggests that $PrAl_2$ and $CaAl_2$ are electronically similar in regard to band structure and both differ in band structure from $GdAl_2$.

Introduction

Compounds represented by the formula RAl_2, where R denotes a rare earth, form in the C15 (cubic Laves phase) structure. (For a comprehensive discussion of the crystallography and magnetism of the RAl_2 series of compounds see Ref. (*1*).) These materials have been extensively studied. Except for $CeAl_2$ and $EuAl_2$ these materials order ferromagnetically at temperatures ranging from 8°K for $TmAl_2$ to 182°K for $GdAl_2$. The effective moment in the paramagnetic state indicates, except for $EuAl_2$, that the rare earth is present as a tripositive ion. Since the R–R separation is large compared to the radial extension of the 4f shell, the dominant magnetic interaction is that which is transmitted via the polarized conduction electrons—the so-called $RKKY$ interaction. $CeAl_2$ represents an exception to this (see below).

$CeAl_2$ is a system of considerable complexity. It has been discussed in detail elsewhere (*2*) and will not be considered further here except to note that because of its small deGennes function, $(g - 1)^2J(J + 1)$, the $RKKY$ is very weak and its magnetism is probably dominated by other interactions, e.g., dipole–dipole interactions.

Eu is present in the elemental state as a dipositive ion, according to Peter and Matthias (*3*). They reached this conclusion based on ESR measurements. Mader and Wallace (*4*) by susceptibility measurements confirmed that Eu in $EuAl_2$ is dipositive, which is also suggested by the large lattice parameter of $EuAl_2$ compared to those of the other RAl_2 systems (*5*). Because of the

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dipositive character of Eu in $EuAl_2$ the electron concentration in $EuAl_2$ is reduced from that in other RAl_2 systems. Inasmuch as the *RKKY* interaction is electron concentration dependent, Mader and Wallace surmised (*4*) that the nature of the magnetic ordering in $EuAl_2$ might be different from that of the other members of the RAl_2 series. This was confirmed; $EuAl_2$ orders antiferromagnetically at temperatures below 30°K.

Mader and Wallace further reasoned (*4*) that the ternary alloys $Eu_{1-x}La_xAl_2$ would develop ferromagnetism because of the increase in electron concentration occurring when dipositive Eu is replaced by tripositive La. This prediction was confirmed in that the ternary systems with $x = 0.6$, 0.8, and 0.9 became ferromagnetic with Curie temperatures of ~3.5, 6, and 11°K, respectively. Thus the coupling could be shifted from antiferromagnetic to ferromagnetic by raising the electron concentration. The quantitative features of this change in sign of the *RKKY* interaction have been analyzed and described by Swift and Wallace (*6*).

Since, as noted, the coupling can be reversed by raising the electron concentration, it appeared that a corresponding effect might occur with lowered electron concentration. Electron concentration can be lowered by replacing the trivalent rare earth ion in a RAl_2 system with a divalent ion, e.g., Ca^{2+}. Since $CaAl_2$ exists in the C15 structure with a lattice parameter within 3% of that of the RAl_2 systems (*7*), extensive solid solubility of RAl_2 and $CaAl_2$ was expected. Therefore it seemed a worthwhile undertaking to prepare some $R_{1-x}Ca_xAl_2$ ternaries and to examine them to ascertain the nature of their magnetic coupling. Two ternary systems were chosen for study—the $Pr_{1-x}Ca_xAl_2$ and $Gd_{1-x}Ca_xAl_2$ systems.

The decision as to which rare earths would be chosen for investigation was not arbitrary; the factors influencing that decision merit discussion. Heat capacity studies of the RAl_2 systems show varied behavior. For $PrAl_2$, the magnetic heat capacity appears as a normal λ-type thermal anomaly (*8*). This is also true for $ErAl_2$ (*9*). However, for $GdAl_2$, the thermal anomaly is not the normal λ-type (*8*). Instead it is spread out over the temperature scale extending from 4 to 170°K. The results cited for $PrAl_2$, $GdAl_2$, and $ErAl_2$ indicate a trend observed for the RAl_2 systems; the magnetic heat capacity behavior changes gradually (*9, 10*) from $PrAl_2$ type at $PrAl_2$ to $GdAl_2$ type at $GdAl_2$ and back to $PrAl_2$ type at $ErAl_2$. The factor or factors responsible for this varying systematic behavior have not yet been elucidated. It appears as if the interaction mechanism varies in a progressive fashion throughout the RAl_2 series, perhaps as a consequence of a varying band structure. For these reasons $GdAl_2$ and $PrAl_2$ were chosen as basis systems for the $R_{1-x}Ca_xAl_2$ ternaries to be investigated magnetically, these two materials representing extrema of the varying magnetic interaction behavior in the RAl_2 series.

Experimental

The rare earth metals were obtained from Research Chemical Inc. and were of 99.9% purity exclusive of nonmetallic impurities.

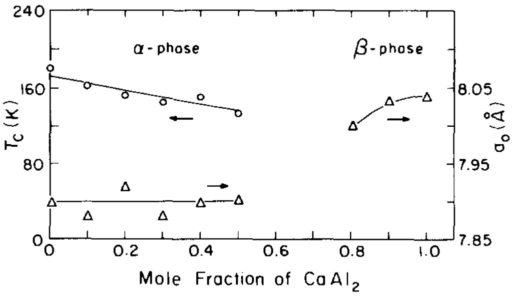

FIG. 1. Lattice parameters and Curie temperatures of $(Ca,Gd)Al_2$ ternaries. There is a miscibility gap between 0.5 and 0.8. The β-phase ternaries do not show magnetic ordering at 4°K.

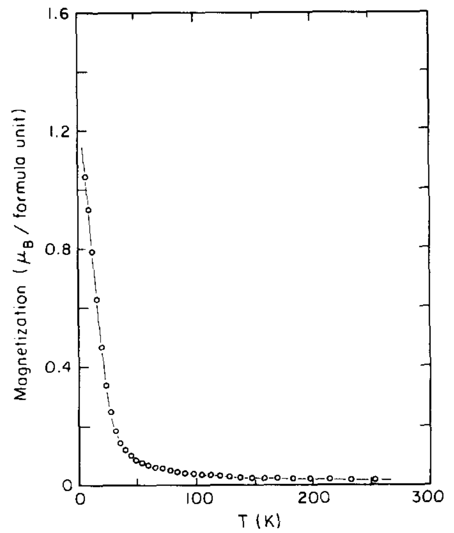

FIG. 2. Magnetization versus temperature for $Pr_{0.5}Ca_{0.5}Al_2$.

The Al was obtained from the Aluminum Company of America and was 99.999% pure. Ca obtained from Foote Mineral was 99.5% pure.

Ca and Pr oxidize readily. They were cut into small pieces, polished with a file, and immersed in parrafin oil. The desired weight of metal was cut off under the oil. The oil was washed off with benzene. Stoichiometric proportions of Ca, rare earth, and aluminum were placed in a high-purity MgO crucible. This crucible was inserted in a tantalum can which was provided with a cap. The loading was carried out in a glovebox under purified helium. The can plus cap was transferred quickly to a specially built arc welder to attach the cap. The welding was done under a bell jar with a purified Ar atmosphere.

The encapsulated mixture of metals was heated with a power supply consisting of an induction coil and a 10-kW 450-kHz generator. Temperature, monitored by an optical pyrometer, was gradually raised to 1200°C. (This temperature was established by trial and error in preliminary work.) Gradual elevation of temperature was required to assure incorporation of Ca in the lattice. The temperature was held at 1200°C for at least an hour. Then the power of the generator was shut off and the sample allowed to cool rapidly. The sample was removed and examined by standard X-ray powder diffraction techniques using a Picker 3488K diffractometer equipped with Cu*Kα* radiation.

Magnetization measurements were carried out using equipment and techniques that are now standard in this laboratory (*11*). Magnetization versus field measurements were carried out at 4.2°K in fields up to about 20 kOe. The magnetization versus temperature behavior was established over the temperature range 4 to 300°K in fields in the range 15 to 20 kOe.

Results

A. Phase Relations and Crystallography

Lattice parameters obtained for the binary systems were in good agreement with literature values: $CaAl_2$, 8.040 Å (8.038 Å); $PrAl_2$, 8.026 Å (8.025 Å); $GdAl_2$, 7.893 Å (7.900 Å). Here the first number

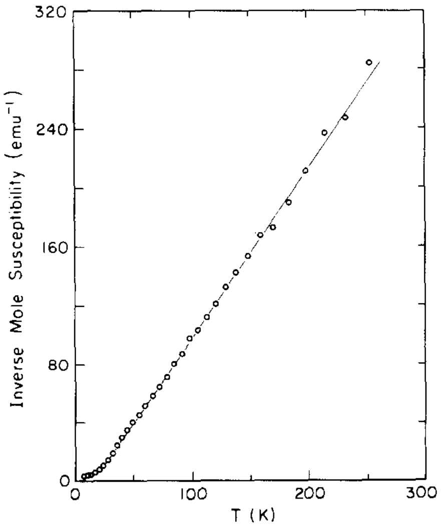

FIG. 3. Inverse molar susceptibility for $Pr_{0.5}Ca_{0.5}Al_2$.

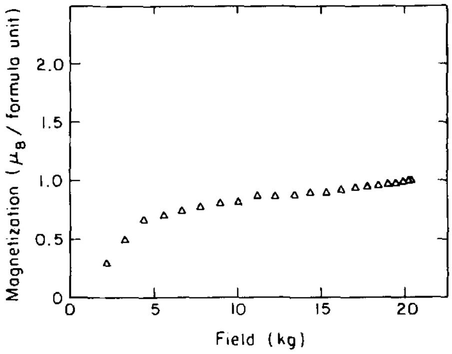

FIG. 4. Magnetization versus field for $Pr_{0.5}Ca_{0.5}Al_2$ at 4.2°K.

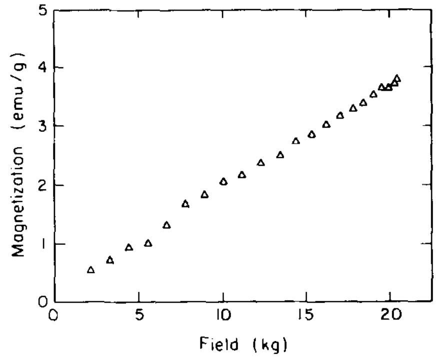

FIG. 5. Magnetization versus field for $Pr_{0.1}Ca_{0.9}Al_2$ at 4.2°K.

is the experimental value, with uncertainty about ±0.002 Å, and the number in parentheses is the lateraturevalue. $PrAl_2$ and $CaAl_2$ appeared by X-ray examination to be completely miscible with lattice parameters following Vegard's rule. In view of the nearly identical lattice parameters a miscibility gap, such as that observed in the $(Gd,Ca)Al_2$ system (see below), could have escaped detection.

$Gd_{1-x}Ca_xAl_2$ shows a miscibility gap from $x = 0.5$ to 0.8 (Fig. 1). The lattice parameter is independent of concentration in the Gd-rich phase (α phase) but varies with composition in the Ca-rich phase (β phase).

B. Magnetic Properties

The results obtained for $Pr_{0.5}Ca_{0.5}Al_2$ (Figs. 2, 3, and 4) are representative of the Pr-rich $(Pr,Ca)Al_2$ ternaries. There is a progressive decline in the Curie temperature (T_c) as Pr is replaced by Ca. In the Ca-rich ternary $Pr_{0.1}Ca_{0.9}Al_2$ there is no indication of magnetic ordering at 4.2°K; magnetization is linear with field (Fig. 5), indicative of a paramagnetic system. The magnetization-field behavior of $Pr_{0.2}Ca_{0.8}Al_2$ (Fig. 6) gives some evidence of metamagnetism with a critical field of about 4 kOe. Magnetic data for the $(Pr,Ca)Al_2$ ternaries are collected in Table 1. The reduced paramagnetic moments for $Pr_{0.1}Ca_{0.9}Al_2$ and $Pr_{0.3}Ca_{0.7}Al_2$ may be a consequence of the tendency toward antiferromagnetic coupling in this composition range.

The $(Gd,Ca)Al_2$ ternaries are paramagnetic at room temperature (as are the

TABLE I

MAGNETIC PROPERTIES OF $Pr_{1-x}Ca_xAl_2$ TERNARIES

x	T_c (°K)	θ (°K)	μ_{eff}/Pr^{3+} atom	Magnetization at 4°K (μ_B/formula unit) H = 20 kOe	$H = \infty$
0 ($PrAl_2$)	37	30	3.46	2.4	2.6
0.1	34	37	2.84	1.7	1.9
0.3	23	18	2.87	1.4	1.6
0.5	17	12	3.46	1.0	1.3
0.7	24	−6	3.50	0.2	0.2
0.9	—	−2	3.46	0.1	—

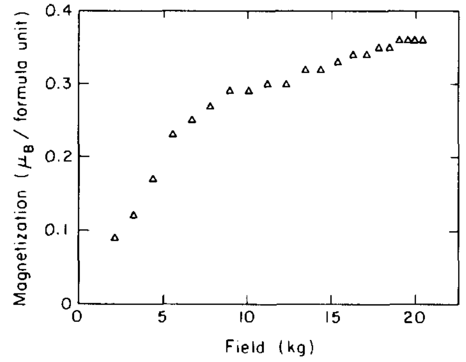

FIG. 6. Magnetization versus field for $Pr_{0.2}Ca_{0.8}Al_2$ at 4.2°K.

corresponding Pr-containing ternaries). The β-phase (Ca-rich) systems remain paramagnetic to the lowest temperature studied. In contrast, the α-phase ternaries (Gd-rich system) order ferromagnetically, the temperature of ordering being reduced as the Ca content increases. The trend of T_c with composition is shown in Fig. 1. A representative field dependence of magnetization is given in Fig. 7. Lack of saturation at the maximum applied field is very evident. The (Pr,Ca)Al_2 system exhibits similar behavior (see Fig. 6).

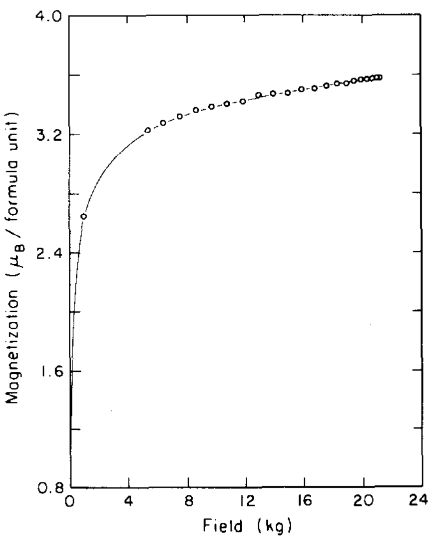

FIG. 7. Magnetization versus field for $Gd_{0.6}Ca_{0.4}Al_2$ at 4.2°K.

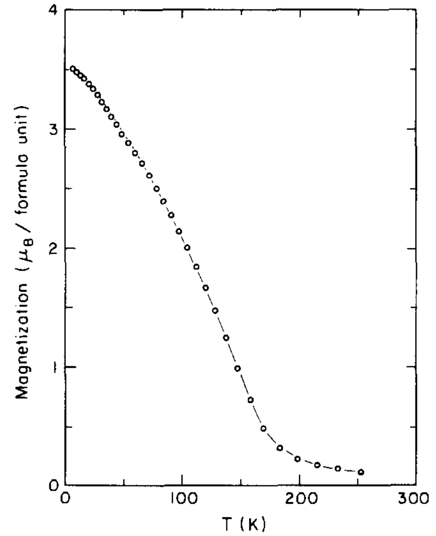

FIG. 8. Magnetization versus temperature for $Gd_{0.6}Ca_{0.4}Al_2$.

Magnetization versus temperature shown in Fig. 8 gives no clear indication of antiferromagnetism. Magnetization shows a rather gradual decline with rising temperature for $Gd_{0.6}Ca_{0.4}Al_2$, and in this respect the ternary system closely resembles $GdAl_2$ (*12*). The gradualness of the demagnetizatin of $GdAl_2$ with rising temperature is the proper accompaniment of the "smeared-out" magnetic heat capacity referred to in the introduction. As indicated earlier, the origin of these unusual features of $GdAl_2$ is yet to be clarified. It is clear, however, that the unusual features are carried over into the α phase of the (Gd,Ca)Al_2 ternaries.

Reciprocal susceptibility versus temperature for $Gd_{0.6}Ca_{0.4}Al_2$, selected to typify the (Gd,Ca)Al_2 ternaries, is shown in Fig. 9. This, in common with the several ternaries studied, fails to show linearity and hence the paramagnetic moment cannot be established. It appears that the features which render the magnetization–temperature behavior anomalous below T_c also influence the susceptibility above T_c so that Curie–Weiss behavior is not observed.

The Curie temperatures and magnetic

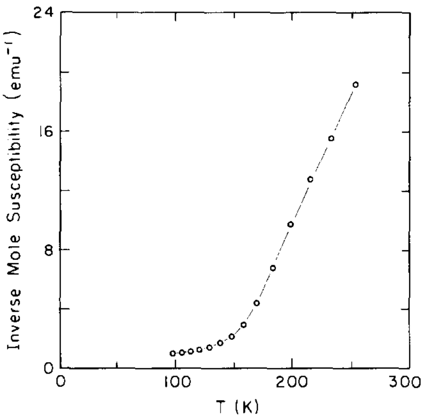

FIG. 9. Inverse molar susceptibility for $Gd_{0.6}Ca_{0.4}Al_2$.

moments measured at 4.2°K and in an applied field of 20 kOe are listed in Table II. The T_c values are also plotted in Fig. 1, as indicated above.

Discussion

Clear evidence for antiferromagnetic coupling in the (Pr,Ca)Al_2 ternaries did not emerge in the investigation. T_c decreased with increasing Ca content. However, this could be ascribed simply to dilution of the magnetic Pr ions. No maximum in susceptibility, characteristic of a Néel point, appeared. There are, however, two indications that there has been a change in the sign of the exchange interaction: (i) the Weiss constant θ is negative for $x > 0.7$ in the $Pr_{1-x}Ca_xAl_2$ ternaries (see Table II) and (ii) the magnetization-field curve for $Pr_{0.2}Ca_{0.8}Al_2$ (Fig. 6) is concave upward at low fields. Both of these are characteristic of an antiferromagnetic system. These results indicate that a careful study of (Pr,Ca)Al_2 ternaries at low field might reveal a Néel point. Such a study was beyond the scope of the present investigation because the sensitivity required to study such a dilute magnetic system under low-field conditions exceeded that of the equipment at hand.

TABLE II

MAGNETIC PROPERTIES OF $Gd_{1-x}Ca_xAl_2$TERNARIES

x	T_c (°K)	Magnetization at 4°K and 20 kOe (μ_B/formula unit)
0.0	182	(7.1)[a,b]
0.1	162	5.45(6.1)
0.2	152	5.32 (6.9)
0.3	145	4.43 (6.3)
0.4	150	3.56 (5.9)
0.5	132	3.30 (6.6)
0.8	Paramagnetic	
0.9	Paramagnetic	
1.0	Paramagnetic	

[a] Taken from Ref. (*12*).

[b] The quantities in parentheses are the moments in μ_B per Gd ion.

The decline in T_c for the α phase of the (Gd,Ca)Al_2 ternaries is in accord with expectation since the magnetic Gd sublattice is being diluted with the nonmagnetic Ca ion. The reduction in T_c is remarkably small compared with that in the (Pr,Ca)Al_2 system. In the latter system T_c is reduced by over 50% when half of the magnetic ions are replaced whereas in the Gd–Ca–Al ternaries replacement to this extent lowers T_c by only 27%. However, the lowering of T_c in the β-phase ternaries is quite drastic. Based on the trends in the α phase one would expect T_c for the β-phase ternary $Gd_{0.2}Ca_{0.8}Al_2$ to be about 115°K. Experiment shows that this material remains paramagnetic to 4.2°K. Thus, there has been a very drastic weakening of exchange in this material compared to that in the α-phase alloys. This implies a significant difference in the electronic makeup of the α and β phases. This is also suggested by the trend of lattice parameters versus composition (see Fig. 1).

The reasoning presented in the preceding paragraph suggests a significant electronic band structure difference between $GdAl_2$ and $CaAl_2$. In view of the complete miscibility of $PrAl_2$ and $CaAl_2$, which implies inter alia a similarity in electronic makeup of these two materials, it can be concluded that $PrAl_2$ and $GdAl_2$ differ significantly in their electronic makeup. It was pointed out in the introduction that the magnetic heat capacities of $PrAl_2$ and $GdAl_2$ differ markedly and this difference could be taken to imply differing band structures for these two materials. This viewpoint is reinforced by the present observation on the two ternary systems. Perhaps the differing band structures of $GdAl_2$ and $PrAl_2$ are a consequence of the much larger magnetic moment of Gd in the rare earth sublattice.

In the $(Gd,Ca)Al_2$ system the α phase corresponds to electron concentrations ranging from 9 to 8.5 and the β phase corresponds to those ranging from 8 to 8.2. In the $(Eu,La)Al_2$ system Mader and Wallace found exchange to be so weak that ordering did not occur at an electron concentration of 8.4. At the phase boundary of the α phase the electron concentration is nearing this critical value. One can postulate that as Ca replaces Gd in $GdAl_2$, exchange is weakened to a point at which ferromagnetic order in the system is no longer energetically favored, and this destabilizes the system so that further Ca cannot be inserted. This then leads to another phase, the β phase, which is stable at higher Ca concentrations and lower electron concentrations.

Acknowledgments

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