Resistivity and magnetization in disordered crystalline compound series $R(Al_xM_{1-x})_2$ (R = rare earth; M = Cu, Co, Fe)

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Electrical resistivity promises to be capable of partly elucidating various important aspects of the phenomenology within the complex field of amorphous-type magnetism in crystalline solids (clamor magnets). For this purpose resistivity measurements were carried out on such partly disordered crystalline pseudobinary compound series as $R(Al_xCo_{1-x})_2$, $R(Al_xFe_{1-x})_2$, and $(R_1,R_2)Al_2$, where R = Gd, Y, or an anisotropic rare earth. Compared to the binaries RAl_2, the relative decrease of resistivity below the magnetic-ordering temperatures of the disordered materials is much smaller for materials based on anisotropic rare earths, and it is also quite weak in those based on Gd. This indicates a considerable influence of exchange fluctuations for the genesis of magnetic clamor states. Selected high-field magnetization measurements are also shown to corroborate a partly disordered magnetic state below the ordering temperature. Some discussion is given to the relationship of crystalline and amorphous magnetic materials.

INTRODUCTION

In this study we search for effects on electrical conductivity of partial site disorder in magnetically ordered, transition-metal substituted pseudobinary compounds based on RAl_2. The interest focuses in particular on a comparison of resistivity and its temperature dependence between systems harboring anisotropic and nonanisotropic rare earths. Neutron diffraction[1] indicates that anisotropic rare-earth moments are partly scattered in direction even below ordering temperatures of the pseudobinaries. Mössbauer-effect measurements[2] show that the rare-earth moments stay approximately constant in magnitude over the pseudobinary composition. The presence of positional entropy in pseudobinary compound series thus creates local fluctuations from site to site in magnetic interaction vectors. This results in a magnetic noise or clamor state, similar to the situation with amorphous rare-earth transition-metal materials.[3]

As there are two major electromagnetic interactions, namely exchange and crystal-field anisotropy, one can broadly discern two major phenomenologies according to whether anisotropy is negligible or not, namely mictomagnetism[4] and randomized anisotropy materials,[1,5] respectively. While not within limiting cases of these phenomenologies, this study, by variation in rare earth, alters the situation from one of predominant exchange noise to a mixture of exchange and anisotropy noise. In particular, resistivity data will be presented for systems of the form $R(Al_xM_{1-x})_2$ and $(R, Y)Al_2$, where R is Gd, Y, Dy, or Er and

M is a $3d$ transition metal. Some magnetization versus field data are also discussed.

The complications stemming from magnetic transition metals have also to be considered. There are some indications for the variability of transition-metal moments in these series. Neutron diffraction[1] has shown that Co develops a moment only beyond 30 mole % $ErCo_2$ in $ErAl_2$-$ErCo_2$. Preliminary results on neutron diffraction in $R(Al_{0.9}Fe_{0.1})_2$ give indication that in the Al-rich compounds the Fe moment must be small at least[6] compared to the usual value found in RFe_2.[7] Neutron diffraction on $R(Al_{0.9}Fe_{0.1})_2$ with R = Ho and Dy indicated no Fe moment within limits of $< 0.3\mu_B$. However, a compound $Dy(Al_{0.5}Fe_{0.5})_2$ showed an Fe moment of order 0.6 μ_B.[8] Magnetization studies on $Gd(Al_xFe_{1-x})_2$ (Ref. 9) indicate a constant Fe moment over the whole series, about $1.6\mu_B$. With R = Y, compounds in the Al-rich region considered here appear to have magnetic Fe.[10]

EXPERIMENTAL

All polycrystalline samples were prepared by induction-melting the stoichiometric amounts of the constituent metals under an argon atmosphere. They were then homogenized at 750 °C in evacuated quartz tubes for about 70 h. X-ray powder patterns exhibited no extraneous reflections. Data for the resistivity were obtained quasicontinuously with slowly changing temperature by means of a four-probe measuring technique applied to bar-shaped samples.

An Au-Fe-Chromel thermocouple was used as a thermometer in the whole temperature range. The accuracy of the temperature measurement is

± 0.5 K in the lowest temperature range and worsens to ± 1.5 K at room temperature. The high-field measurements discussed also in this work were performed on a pulsed field magnetometer[11] at 4.2 K in fields up to 1.43×10^7 A/m. To prevent complications due to eddy currents, these measurements were performed on powdered samples.

RESULTS

All compounds of the present study crystallize with the $C15$ structure. The temperature dependence of resistivity for the compounds investigated is presented in Fig. 1. Arrows indicate the ordering temperatures. The aim of Fig. 2 is to show how one can understand the temperature dependence of resistivity in RAl_2. Assuming Matthiessen's rule, one can consider the total resistivity in RAl_2 to be a sum of three contributions

$$\rho = \rho_0 + \rho_{ph} + \rho_{mag} , \qquad (1)$$

where ρ_0 is the residual resistivity, ρ_{ph} is the contribution caused by electron-phonon scattering processes, and ρ_{mag} is the contribution caused by disordered localized magnetic moments. In a simplified model,[12] it can be shown that ρ_{mag} becomes temperature independent in the high
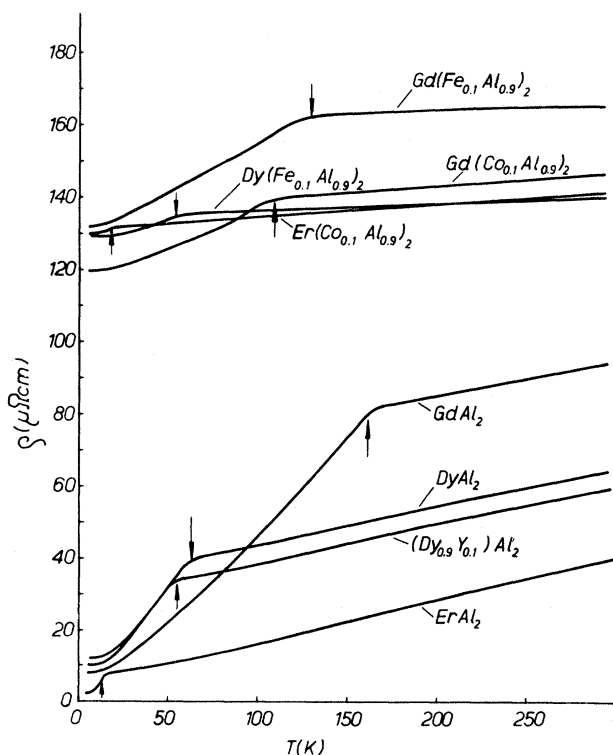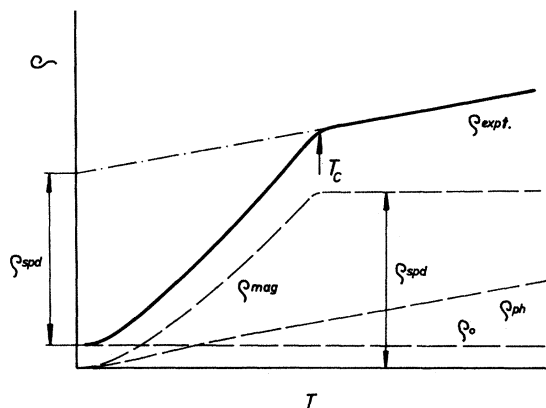
FIG. 2. Schematic description of the temperature dependence of resistivity typical for RAl_2.

(paramagnetic) temperature range. In this case it is common to call this term spin-disorder resistivity or ρ_{spd}. Summing over these different contributions one obtains plots of ρ vs. T similar to the ones found in the compounds investigated. As shown in the schematic figure one can obtain ρ_{spd} from experimental measurements by an extrapolation procedure. Experimental values of ρ_0 and ρ_{spd} are collected in Table I. Also a ratio r is shown, defined as the ratio between ρ_{spd} of the magnetically disordered compound and the ordered compound RAl_2. Two facts are apparent: (1) Dramatic increase of ρ_0 (residual resistivity) in the case of partial Fe or Co substitution for Al in RAl_2, and (2) the pronounced decrease of ρ_{spd} in the pseudobinaries in which 10% of Al is substituted by Fe or Co. The magnitude of r gives a measure of this decrease.

In the series based on $GdAl_2$ [$Gd(Al_xM_{1-x})_2$], values of r are relatively high with $M = Cu$ but find a minimum with $M = Co$. A similar trend is observed in ordering temperatures (Table I). Values of r are considerably lower in the case of $Dy(Al_xFe_{1-x})_2$. However, partial substitution for Dy by Y ($Dy_{0.9}Y_{0.1}Al_2$) has a relatively small effect on r. The strongest effect on depressing r is found with $Er(Al_{0.9}Co_{0.1})_2$.

As mentioned, a transition-metal substitution causes a strong influence on magnetic behavior. In Fig. 3 it is shown that the Fe-based compounds $Dy(Al_{0.9}Fe_{0.1})_2$ and $Ho(Al_{0.9}Fe_{0.1})_2$ are, even in pulsed fields up to 1.43×10^7 A/m, much less saturated than the corresponding RAl_2 compounds.

DISCUSSION

It is remarkable that in the Fe- or Co-substituted RAl_2 compounds, $\rho_{4.2}$ is extremely high ($\rho_{4.2}$ represents the resistivity at liquid-helium temperatures). In a first approximation one can assume

FIG. 1. Temperature dependence of resistivity of some selected RAl_2, $(R_1,R_2)Al_2$, and $R(Al_xM_{1-x})_2$ compounds.

TABLE I. Electrical resistivity and magnetic parameters of materials based on $GdAl_2$, $DyAl_2$, and $ErAl_2$. r is the ratio of the spin-disorder resistivities of the peudobinary to the binary parent compound. T_C's were obtained from the breaks in the ρ vs T curves. $d\rho/dT$ was obtained between 180 and 250 K.

Material	ρ_0 ($\mu\Omega$ cm)	ρ_{spd} ($\mu\Omega$ cm)	r	$d\rho/dT$ ($\mu\Omega$ cm/K)	T_C (K)
$GdAl_2$	8	59	(1)	0.096	165
$Gd(Al_{0.9}Fe_{0.1})_2$	132	31	0.53	0.017	130
$Gd(Al_{0.9}Co_{0.1})_2$	120	20	0.34	0.040	110
$Gd(Al_{0.9}Cu_{0.1})_2$	42	46	0.78		145
$DyAl_2$	10	24	(1)	0.099	65
$Dy(Al_{0.9}Fe_{0.1})_2$	129	5.3	0.22	0.020	58
$Dy_{0.1}Y_{0.1}Al_2$	12	17	0.71	0.111	52
$ErAl_2$	1.5	5	(1)	0.115	12
$Er(Al_{0.9}Co_{0.1})_2$	130	1	0.2	0.039	14

that this value is equal to ρ_0, the residual resistivity at $T = 0$ K. ρ_0 indicates temperature-independent scattering processes (e.g., Coulomb scattering on substituted atoms, dislocations, etc., and also the scattering processes on domain walls in the case of magnetic order at $T = 0$). Each kind of substitution causes an increase of ρ_0 relative to the boundary phase. In contrast to the small increase for Y substitution in $DyAl_2$ and Cu substitution in $GdAl_2$, substitution of 10 mole% RFe_2 or 10 mole% RCo_2 in RAl_2 causes an increase of ρ_0 of more than 10 times the value of the boundary phase. This unusually large increase of ρ_0 cannot be explained only by assuming weak Coulomb scattering processes. The substitution of a $3d$ metal such as Fe or Co in RAl_2 must have a dramatic influence on the electronic state.

For the binaries, the spin-disorder resistivity

FIG. 3. M vs H curves at 4.2 K from polycrystalline; × $HoAl_2$, ● $DyAl_2$, ■ $Ho(Al_{0.9}Fe_{0.1})_2$, and ▲ $Dy(Al_{0.9}Fe_{0.1})_2$.

is given by[12]

$$\rho_{spd} = \frac{3\pi N m^*}{2\hbar e^2 E_F} G^2(g-1)^2 J(J+1),\qquad (2)$$

where N is the number of rare earths per unit volume, m^* is the electronic effective mass, E_F is the Fermi energy, g the Lande' factor, G the exchange coupling constant, and J the total angular momentum of the rare earth. Thus ρ_{spd} in the binaries should vary as $(g-1)^2 J(J+1)$, the de-Gennes factor. This is tested in Table II. The tendencies are as expected; however, the spin-disorder resistivity contribution for $ErAl_2$ seems low. Part of this effect could be due to some loss of spin-disorder resistivity in the paramagnetic phase, as the crystal-field levels depopulate at low temperatures. We have performed a calculation of this based on the method of Hirst[13] using a crystal-field scheme comparable to that of Purwins et al.[14] One finds that about 25% of the spin-disorder resistivity should be lost by T_C.

The spin-disorder resistivity of $Dy_{0.9}Y_{0.1}Al_2$ can be compared to that of $DyAl_2$ via the model developed by Dekker[12] for rare-earth alloys. One finds that

$$\frac{\rho_{spd}(Dy_xY_{1-x}Al_2)}{\rho_{spd}(DyAl_2)} = \frac{x(1+xJ)}{(1+J)}.\qquad (3)$$

Thus, the predicted r is 0.82, while the observed

TABLE II. Relative experimental ρ_{spd} versus relative deGennes factor $(g-1)^2 J(J+1)$ in some RAl_2 (both normalized to $GdAl_2$).

	ρ_{spd}/N_1	$(g-1)^2 J(J+1)/N_2$
$GdAl_2$	(1)	(1)
$DyAl_2$	0.41	0.45
$ErAl_2$	0.08	0.16

value is 0.71, in fairly good agreement. The question why partial Y substitution does not have a pronounced effect on r appears obviously related with the similarity of Y and Dy, the rare earth in question. In similar systems it is common experience that the magnetic structures (even complicated modulated ones) are often not much influenced by partial substitutions, as exchange is "imprinted" on the total crystal by a polarized pattern of conduction electrons.

For the $R(Al_xM_{1-x})_2$ pseudobinaries, the decrease in ρ_{spd} upon substitution could be due to some radical change in the parameters of Eq. (2). For example, ESR measurements on $Gd(Al_xCo_{1-x})_2$ have shown[15] that the exchange parameter G decreases upon initial Co substitution in $GdAl_2$, resulting in a decrease in Curie temperature. However, the Curie temperatures tabulated for the anisotropic R pseudobinaries show a generally smaller fractional change from the corresponding RAl_2.

Another explanation is a breakdown of the additive rule [Eq. (1)]. This has been seen in amorphous materials; in a-Gd_7Ni_3 and several other representatives,[16] there is no discernable ρ_{spd} contribution. $d\rho/dT$ (at high temperature) is minimal (and positive or negative) so that the phonon contribution is also not an independent entity and ρ_0 is quite large. In a-$GdNi_3$ and related alloys,[17] a similar effect is observed. Theory developed in this latter work suggests that local spin correlations can lead to either positive or negative contributions to the resistivity on ordering. In crystalline pseudobinaries, the $Gd(Ni_xCu_{1-x})_2$ system[18] exhibits little variation in $d\rho/dT$, a small increase in ρ_0, and a relatively constant ρ_{spd}. In $TbAg_xIn_{1-x}$ (Ref. 19), $d\rho/dT$ is fairly constant, ρ_0 increases sharply with substitution, and ρ_{spd} varies irregularly with composition. However, in this case superzone boundaries associated with the antiferromagnetic ordering[20] may tend to decrease the observed ρ_{spd}. The transition-metal system $R_6(Mn_xFe_{1-x})_{23}$ (Ref. 21) might appear similar to the one seen here; $d\rho/dT$ is nearly constant (usually negative), ρ_0 is large, and ρ_{spd} is missing in the pseudobinary region.

In the present work, the sharply increasing ρ_0 and decreasing $d\rho/dT$ (Table I) with substitution suggest an intermediate situation between the binaries and amorphous materials. One can then try to correlate the decrease in ρ_{spd} with either the increase in ρ_0 or the decrease in $d\rho/dT$. In Fig. 4, we plot r vs ρ_0 for the compounds investigated in this study. As expected, the greater the residual resistivity, the smaller the spin-disorder resistivity. A similar correlation holds with r and $d\rho/dT$ (not shown). Some care must be taken
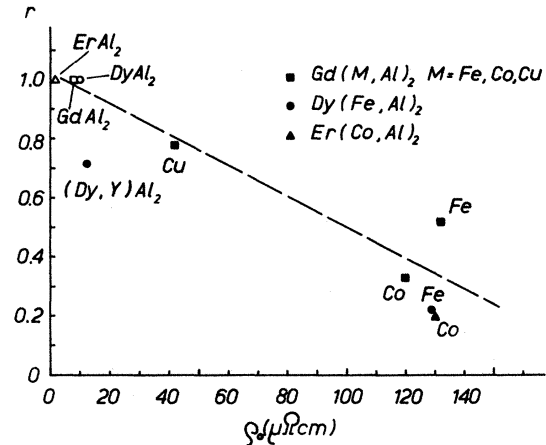

FIG. 4. Ratio of the spin-disorder resistivities of the substituted compounds to the binaries (r) vs ρ_0.

in interpreting the ρ_{spd} vs ρ_0 plot, since the experimental determinations of ρ_{spd} and ρ_0 are related.

Intermetallics based on anisotropic magnetic elements are well known as being capable of exhibiting high values of average scatter angle between ordered magnetic moments as well as dramtic increases of intrinsic hardness upon introduction of positional entropy. The disorder associated with moment scatter was expected to decrease r. Such an effect is indeed observed when respective values for $Gd(Al_xFe_{1-x})_2$ and $Dy(Al_xFe_{1-x})_2$ are compared (Gd analogs are not anisotropic). Contrarily, only little difference in r is observed between $Gd(Al_xCo_{1-x})_2$ and $Er(Al_xCo_{1-x})_2$. However, G decreases on Co substitution in $GdAl_2$, but the essentially constant Curie temperatures which occur for Co substitution in the Er analog may imply little change in G for this system.

A major finding of this work therefore concerns the fact that sizable reductions in values of r are also observed in analogous materials based on Gd which have not shown major moment scatter or intrinsic hardness effects to date. One possibility is to consider that the r reductions in the Gd-based materials are due to resultant scatter with small critical fields for complete moment alignment. However, in the a-$GdNi_x$ series, applied fields cause only small changes in the spin-disorder resistivity (both positive and negative depending on x). The enormous increases in ρ_0 relative to the binaries suggest resonance scattering of electrons at the Fermi level by transition-metal atomic d levels near the Fermi surface.[22] In the strong scattering case (Ref. 23), $d\rho/dT$ may be positive or negative, thermal disorder actually enhancing conduction-electron flow in the latter.

Since a dominant effect appears to be due to d-level scattering, the strongly magnetic iron in $Gd(Al_{0.9}Fe_{0.1})_2$ may be due to a shift in the d levels as compared to the other substituted transition-metal compounds and lead to an enhanced r. Exchange modifications of the conduction band have been implied in studies on the RAl_2.[24]

The magnetization studies apparently do show the effects of lowered rare-earth crystal-field symmetry. In Fig. 5, the differences in magnetization between the RAl_2 binaries and the iron-substituted materials are shown. An approximately linear decrease with field is observed beyond 2×10^6 A/m. The extrapolated fields where substituted materials reach moments comparable to the ordered binary compounds approach values of the order of the exchange fields.[25] The maximum possible Fe contribution to the moment is about $0.3 \mu_B$ per formula unit, far less than the zero field extrapolated differences of $1.3 \mu_B$ per formula unit for $DyAl_2$-$Dy(Al_{0.9}Fe_{0.1})_2$, or $0.8 \mu_B$ per formula unit for $HoAl_2$-$Ho(Al_{0.9}Fe_{0.1})_2$. Contrarily, $Gd(Al_{0.75}Fe_{0.25})_2$ exhibits[9] a constant magnetization difference with $GdAl_2$ to within $0.1 \mu_B$ per formula unit for fields to 1.2×10^7 A/m.

A distributed coercivity from the pulsed field cannot be responsible for the moment differences, since the Ho analog shows almost no intrinsic coercivity compared to the Dy analog. Since the moments in the binaries extrapolated to zero field correspond to the residual moments for cubic, polycrystalline materials $(M_0/M_s \approx 0.83)$,[26] the reduced extrapolated values in the pseudobinaries suggest a lower-than-cubic symmetry. The value of M_0/M_s for $Dy(Al_{0.9}Fe_{0.1})_2$ is about 0.7, intermediate between the cubic result and the uniaxial value 0.5 $(K_1 > 0)$.[27]

The incremental work done by the external field can be calculated to estimate the added anisotropy in the pseudobinaries. In both cases, we assume $\mu_{Fe} = 0.3 \mu_B$ per formula unit. For the Dy pair, the incremental work associated with the polycrystalline pseudobinary is about 1.7×10^7 ergs/cm^3. For the Ho analogs, the incremental work is somewhat less at 1.0×10^7 ergs/cm^3. For comparison, the uniaxial contribution to the work of Sm in $SmCo_5$ (in this case, K_1) is calculated to be[28] about 2.0×10^8 ergs/cm^3 at 4.2 K. For a polycrystalline material, one would measure approximately one-half the work,[27] or 1.0×10^8 ergs/cm^3.
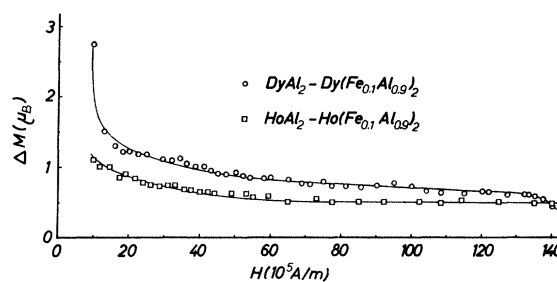

FIG. 5. Difference in magnetization between some RAl_2 binaries and $R(Al_{0.9}Fe_{0.1})_2$ versus applied field.

Thus, the additional crystal-field anisotropy in the pseudobinaries is on the order of 15% of the $SmCo_5$ anisotropy.

Although these changes in anisotropy imply a substantial variation in the crystal-field schemes relative to the binaries, no change attributable to spin-disorder resistivity is observed above T_C for $Er(Al_{0.9}Co_{0.1})_2$. The paramagnetic spin-disorder resistivity depends on the crystalline wave functions and degeneracies in a complex way, and a decrease may not occur. However Co substitution is expected to increase the anisotropy in the same way as Fe substitution, since the extrapolated moments in $Er(Al_xCo_{1-x})_2$ decrease with initial Co substitution[29] as in the $R(Al_xFe_{1-x})_2$ binaries shown here. In fact, for the heavy rare earths Tb, Dy, Ho, and Er, the RAl_2 compounds substituted by transition metals Fe, Co, and Ni always show an initial decrease in extrapolated moment except for $Ho(Al_xCo_{1-x})_2$ and $Er(Al_xNi_{1-x})_2$.[30]

Future experiments should concern themselves with systematic and precise neutron diffraction measurements and studies of the effects on resistivity of partial field alignments of the scatter cones. Also a wider range of materials especially ones with a lack of d-level scattering should be of interest. Theoretical modeling may take advantage of the ground-breaking work on amorphous materials.[3]

ACKNOWLEDGMENTS

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