JOURNAL OF SOLID STATE CHEMISTRY 3, 180–183 (1971)

Reversal of Coupling in Intermetallic Compounds Containing Two Rare Earth Elements*

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Received September 2, 1970

The reversal in coupling (from antiferromagnetic to ferromagnetic order with increasing x) in $Eu_xLa_{1-x}Al_2$ ternaries is successfully analyzed in terms of the RKKY formalism. The Fermi wavevector k required to account for the behavior of these ternaries is $k = 0.94\,k_0$, which is in close agreement with the k-value previously obtained for $GdAl_2$ and $GdAl_2$-based ternaries from NMR work. The similarity of behavior of $Gd_{0.1}La_{0.9}Al_2$ and $Eu_{0.1}La_{0.9}Al_2$ and their observed Curie temperatures can also be understood using the same theoretical framework and approximately the same k-values.

Introduction and Background

The lanthanide elements, here designated Ln, form several series of binary and pseudobinary intermetallic compounds which crystallize in the cubic Laves phase structure (prototype $MgCu_2$ structure). Among the more intensely investigated systems of this type have been the $LnAl_2$ binary and $Ln_xLn'_{1-x}Al_2$ pseudobinary intermetallics (*1–3*). Aluminum is responsible to a large extent for the interest in these compounds since its core is nonmagnetic and has the same valence state as most lanthanide elements. Thus, relatively unambiguous interpretation of bulk magnetic properties has been possible. In addition, ^{27}Al NMR measurements have yielded valuable information on the exchange interactions between the conduction electrons and the localized rare earth moments (*4, 5*).

Williams, et al. (*1*) first characterized the bulk magnetic properties of eleven $LnAl_2$ binary compounds and several pseudobinary systems. These investigators reported that the binary compounds order ferromagnetically below room temperature with $GdAl_2$ exhibiting the strongest coupling (Curie temperature ~170°K). However, the pseudobinary $Ln_xLn'_{1-x}Al_2$ systems exhibited either ferromagnetic or ferrimagnetic coupling depending on the particular L–S coupling scheme in Ln and Ln'. Later, Swift and Wallace (*2*) verified the findings of Williams, et al. and investigated twelve additional pseudobinary systems. The results of both of these investigations clearly indicated that the dominant mode of exchange in these systems is one in which the rare earth spins couple ferromagnetically. This model adequately explains the observed ferromagnetism in trivalent $LnAl_2$ binary compounds and the ferrimagnetism in $Ln_xLn'_{1-x}Al_2$ systems having rare earths with different L–S coupling schemes (*6*).

There exists, however, a different coupling mode in $EuAl_2$ and in some of the $Eu_xLa_{1-x}Al_2$ pseudobinaries. Mader and Wallace (*3*) reported that europium, unlike the other lanthanide elements, was divalent in these compounds and that $EuAl_2$ orders antiferromagnetically at 30°K. Furthermore, the $Eu_xLa_{1-x}Al_2$ pseudobinaries exhibited a shift from antiferromagnetic to ferromagnetic coupling with increasing lanthanum concentration. A paramagnetic phase existed between the two ordered phases (see data in Table I). Since the La^{3+} core carries no moment, it was concluded in the earlier work that the smaller electron-to-atom ratio in $EuAl_2$ gave rise to antiferromagnetic coupling and that lanthanum, by raising the electron concentration, induced the shift back to ferromagnetic coupling. It is of interest to ascertain whether or not present concepts of exchange in these materials are able to provide a basis, hopefully a quantitative one, for understanding the observed reversal of coupling.

*This work was assisted by grants supplied by the National Aeronautics and Space Agency and the U.S. Atomic Energy Commission.

TABLE I

SUMMARY OF THE PROPERTIES OF $Eu_xLa_{1-x}Al_2$ COMPOUNDS (3)

	Lattice parameter	μ_{eff}	T_N (°K)[a]	T_N' (°K)	T_c (°K)[b]
$EuAl_2$	8.123	7.88	15	30	—
$Eu_{0.8}La_{0.2}Al_2$	8.128	7.95	14	30	—
$Eu_{0.6}La_{0.4}Al_2$	8.133	8.10	—	paramagnetic	—
$Eu_{0.4}La_{0.6}Al_2$	8.136	7.85	—	—	<4°K
$Eu_{0.2}La_{0.8}Al_2$	8.140	7.85	—	—	6
$Eu_{0.1}La_{0.9}Al_2$	8.142	7.80	—	—	11
$LaAl_2$	8.145	Pauli paramagnetic	—	—	—
$Gd_{0.1}La_{0.9}Al_2$	8.11	—	—	—	24

[a] Néel Temperatures.
[b] Curie Temperatures.

In this paper, the results of appropriate calculations for $EuAl_2$, $LaAl_2$, $Eu_{0.1}La_{0.9}Al_2$, $Gd_{0.1}La_{0.9}Al_2$, and several other $Eu_xLa_{1-x}Al_2$ pseudobinary compounds are reported and discussed. Results support the qualitative suggestions advanced by Mader and Wallace and the general concept of the exchange coupling operating in rare earth compounds combined with a nonmetallic partner.

Theory

It is generally accepted that the dominant mechanism of magnetic coupling in the rare earths, and in intermetallics in which a rare earth is combined with a nonmagnetic partner, develops out of the exchange between conduction electron spins and the localized core spins of the rare earths (7–9). This exchange provides a coupling mechanism for the core electron spins, the so-called RKKY interaction. The Hamiltonian for core-conduction electron exchange may be expressed as

$$\mathscr{H} = -\Gamma \mathbf{s}_e \cdot \mathbf{S}_{RE}, \qquad (1)$$

where $\mathbf{s}_e$ and $\mathbf{S}_{RE}$ are the spin vectors of the conduction electrons and core spins, respectively, and Γ is the exchange integral. The conduction electrons are polarized by this exchange. To the second-order this polarization is proportional to

$$F(x) = \frac{x\cos x - \sin x}{x^4}; \qquad x = 2k_F R_{ij}, \qquad (2)$$

where k_F is the Fermi wavevector and R_{ij}'s are interatomic distances between core spins. deGennes (10) has shown that the Curie constant, θ, is related to the conduction electron polarization as follows:

$$\theta = \frac{-3\pi n^2 \Gamma^2}{4k_B E_F}(g-1)^2 J(J+1) \sum_{i \neq j} F(2k_F R_{ij}). \qquad (3)$$

Here n is the number of conduction electrons per atom, k_B is the Boltzmann constant, E_F the Fermi energy, g the Lande factor, J is the total angular momentum of the ion core and the summation is termed the RKKY sum. The summation in (3) is carried out over all neighbours excluding the reference site. As such, (3) may be viewed as the molecular field at the reference site arising from the conduction electron polarization. It is important to note that the sign of θ is solely dependent on the sign of this summation. This summation is obviously negative for ferromagnetic exchange and positive for antiferromagnetic exchange.

Results

The RKKY summations for $EuAl_2$ and $LaAl_2$ are shown in Fig. 1. These summations were carried out over the first 35 nearest neighbors which encompasses a sphere of radius $3a_0$ about the reference site. The summations were evaluated as a function of k/k_0 where k_0 is the free electron Fermi wavevector. Although $LaAl_2$ is Pauli paramagnetic, the summation for it may be obtained and may be regarded as the prototype for all trivalent $LnAl_2$ compounds. It is obvious from Fig. 1 that the RKKY function for $EuAl_2$, having an electron-to-atom ratio of 2.66, is significantly different from that occurring in $LnAl_2$ compounds with electron-to-atom ratio of 3.00. In $EuAl_2$ the sum is positive

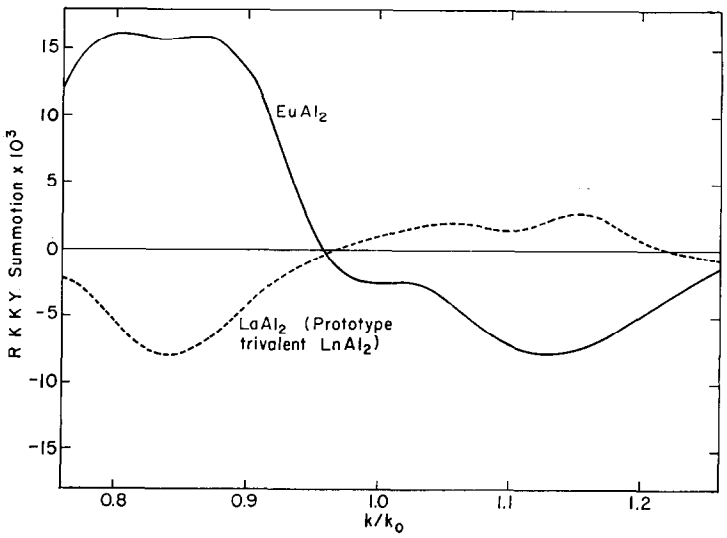

FIG. 1. RKKY sums for $EuAl_2$ and $LaAl_2$ versus k/k_0. k_0 is the free electron Fermi radius and k is the effective Fermi radius.

(antiferromagnetic exchange) between $k = 0.70\ k_0$ and $0.96\ k_0$. On the other hand, the sum for trivalent $LnAl_2$ binaries is negative from $k = 0.70\ k_0$ to $0.96\ k_0$ and positive from $k = 0.96\ k_0$ to $1.22\ k_0$. These shifts in sign, and hence magnetic coupling, are a result of the difference in electron concentration for $EuAl_2$ and the trivalent $LnAl_2$ binaries. Buschow, et al. in their study of $GdAl_2$ (*11*) provided an excellent accounting for the observed Curie temperature and Knight shift with $k = 0.94\ k_0$ for $GdAl_2$. From Fig. 1 it is seen that for $k = 0.94\ k_0$ exchange is expected to be antiferromagnetic for $EuAl_2$ and ferromagnetic for corresponding compounds containing Ln^{3+}.

The results of the RKKY summations in $Eu_xLa_{1-x}Al_2$ pseudobinaries are reported in Table II. For these calculations, it was assumed that the lanthanides were randomly distributed in the various shells surrounding the reference Eu^{2+} site. As might be anticipated from the results for $EuAl_2$ and $LaAl_2$, a progressive shift in the region of ferromagnetic exchange occurs as Eu^{2+} is replaced with La^{3+}. The shift from antiferromagnetism to paramagnetism was observed by Mader and Wallace (*3*) to occur at about $Eu_{0.7}La_{0.3}Al_2$. Paramagnetism occurs at the point where the RKKY summation changes sign. The results of Mader and Wallace can be rationalized in terms of the calculations shown in Table II if k is taken to be $0.92\ k_0$. This value is very close to that employed by Buschow, et al. ($k = 0.94\ k_0$), referred to above, in successfully accounting for the bulk magnetic and NMR characteristics of both $GdAl_2$ and a large number of ternary systems based upon $GdAl_2$ (*11*). The close agreement between k needed to systematize the present results and that found by Buschow, et al. strongly supports the conclusion of Mader and Wallace, which was based upon qualitative considerations, and provides additional

TABLE II

REGIONS OF FERROMAGNETIC EXCHANGE IN $Eu_xLa_{1-x}Al_2$

	Intermetallic compounds	
Compound	Electron to atom ratio	Region of ferromagnetic exchange (negative RKKY sum)[a]
$EuAl_2$	2.66	$0.96 \rightarrow 1.28\ k_0$
$Eu_{0.9}La_{0.1}Al_2$	2.70	$0.95 \rightarrow 1.27\ k_0$
$Eu_{0.8}La_{0.2}Al_2$	2.73	$0.93 \rightarrow 1.25\ k_0$
$Eu_{0.7}La_{0.3}Al_2$	2.76	$0.90 \rightarrow 1.22\ k_0$
$Eu_{0.6}La_{0.4}Al_2$	2.80	$0.88 \rightarrow 1.19\ k_0$
$Eu_{0.5}La_{0.5}Al_2$	2.83	$0.86 \rightarrow 1.16\ k_0$
$Eu_{0.4}La_{0.6}Al_2$	2.87	$0.83 \rightarrow 1.18\ k_0$
$Eu_{0.3}La_{0.7}Al_2$	2.90	$0.79 \rightarrow 1.08\ k_0$
$Eu_{0.2}La_{0.8}Al_2$	2.93	$0.74 \rightarrow 1.02\ k_0$
$Eu_{0.1}La_{0.9}Al_2$	2.96	$0.71 \rightarrow 0.97\ k_0$
$LaAl_2$	3.00[b]	$0.70 \rightarrow 0.96\ k_0$

[a] The values of k_0 to the left and right of these regions correspond to regions of stable antiferromagnetic exchange (positive RKKY summation).

[b] Prototype for all trivalent $LnAl_2$ compounds.

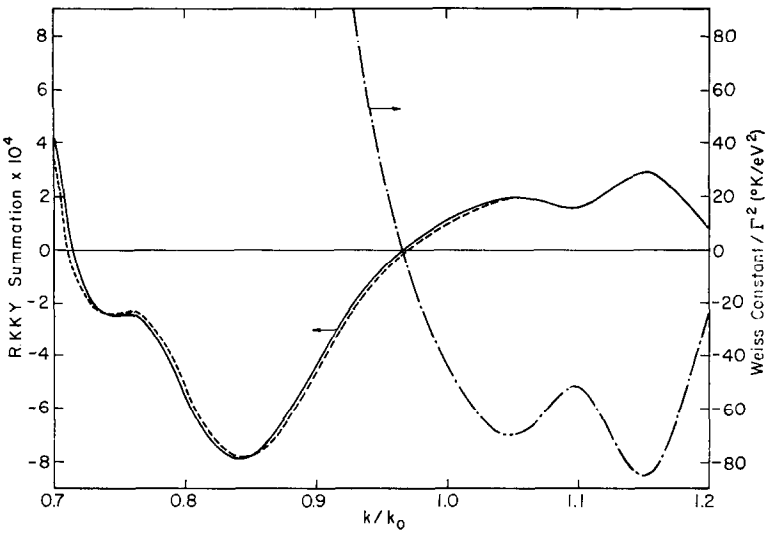

FIG. 2. RKKY sums and variation of θ/Γ^2 for $Gd_{0.1}La_{0.9}Al_2$ (solid curve) and $Eu_{0.1}La_{0.9}Al_2$ (dashed curve).

evidence to affirm that the RKKY mechanism is indeed the dominant interaction in intermetallics involving a rare earth in chemical union with a nonmagnetic partner.

The properties of $Eu_{0.1}La_{0.9}Al_2$ and $Gd_{0.1}La_{0.9}Al_2$ in relation to the theoretical framework just presented merit comment. These compounds have electron-to-atom ratios of 2.96 and 3.0 and exhibit Curie points at 11°K and 24°K respectively (Table I). Noting the similarity in electron-to-atom ratios and that Eu^{2+} is isoelectronic with Gd^{3+}, the similarity of properties of these compounds is not unanticipated. The RKKY summation for these compounds is shown in Fig. 2, together with variation in θ/Γ^2. The latter data were obtained from Eq. 3 by using $g = 2$, $J = 7/2$, $E_F = h^2k^2/2m$ and the literature value (*10*) for Γ in $GdAl_2$ ($\Gamma = -0.9$ ev). The Curie temperatures for $Eu_{0.9}La_{0.1}Al_2$ and $Gd_{0.9}La_{0.1}Al_2$ are accounted for (Fig. 2) with $k = 0.96\ k_0$ and $k = 0.95\ k_0$, respectively, in close agreement with the values of k referred to above.

In closing, it is appropriate to direct attention to the significance of k values differing from k_0. The RKKY formation is developed using a free electron model. Of course rare earth systems do not conform to a free electron description. Departures from free electron behavior are taken into account by allowing k to deviate from k_0, a procedure which seems somewhat less than satisfactory but which has proved effective (*11*) in dealing with the NMR characteristics of rare earth systems.

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