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NMR and Magnetic Susceptibility of $Gd_2Cu_6Al_{11}$ and $Gd_2Co_6Al_{11}$ Intermetallic Compounds*

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^{27}Al Knight shifts and the magnetic susceptibilities of $Gd_2Cu_6Al_{11}$ and $Gd_2Co_6Al_{11}$ are reported. The contributions to the magnetic susceptibility are Curie–Weiss terms expressing the paramagnetism of the localized *f* and *d* electrons of Gd and Co atoms, and a temperature-independent term. The phenomenological exchange constant γ_{sf} between 4*f*-electron spins and conduction electron spins in both the compounds is derived to be -1.26×10^{-3} eV. In the $Gd_2Co_6Al_{11}$ system the Co moment couples with the ^{27}Al nucleus through two mechanisms: (1) through direct overlap between the Co 3*d* orbitals and the Al core electrons, leading to core polarization, and (2) through conduction electron polarization. The corresponding phenomenological exchange constants γ^{i}_{sd} and γ^{e}_{sd} are derived to be -0.0375 and 1.33×10^{-3} eV, respectively.

1. Introduction

The rare earths form numerous intermetallic compounds (see, e.g., Ref. (*1*)). One of the common stoichiometries (*2*) is represented by the formula R_2T_{17}, where *R* represents a rare earth and *T* is another metallic element, usually a 3*d* transition metal. The R_2T_{17} compounds occur (*2*) in either the Th_2Ni_{17} or the Th_2Zn_{17} structure types, depending upon the nature of *R* and *T*.

Ternary intermetallics containing rare earths have been extensively investigated (*2, 3*) in the past decade because of their varied and interesting magnetic behavior. The present paper is concerned with ^{27}Al NMR characteristics of two Al-containing systems, $Gd_2Co_6Al_{11}$ and $Gd_2Cu_6Al_{11}$. The former may be regarded as derived from Gd_2Co_{17} by partial replacement of Co with Al; the latter may be regarded as $GdCo_6Al_{11}$ in which the Co is replaced by Cu. The choice of stoichiometry of the ternary was dictated by the need to have as large a concentration of Al as possible while preserving the R_2T_{17}-type structure. Both ternaries occurred in the Th_2Ni_{17} structure.

A comparative investigation of $Gd_2Co_6Al_{11}$ and $Gd_2Cu_6Al_{11}$ seemed of interest in that the aspects of the magnetic behavior which are peculiar to magnetic Co, in contrast with nonmagnetic Cu, might be revealed.

2. Experimental

The compounds were prepared by induction melting together stoichiometric proportions of

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the elements in a water-cooled copper boat. During the preparation procedure the samples were kept under a stream of purified Ar. The existence of these ternaries in the hexagonal Th_2Ni_{17} structure was confirmed by conventional X-ray powder diffraction analysis, and the lattice parameters are as follows: a = 8.923 Å, c = 9.016 Å for $Gd_2Cu_6Al_{11}$; and a = 8.723 Å, c = 8.931 Å for $Gd_2Co_6Al_{11}$, respectively.

The magnetic susceptibility was measured between 80 and 1200°K in a field at 9450 Oe, using a Faraday magnetic balance with a sensitivity of 10^{-8} emu/g.

The NMR spectra of ^{27}Al nuclei were recorded on powders in a 9212-MHz INM-3 spectrometer, improved by a broad-line attachment JNM-BH-2. Spectra were obtained at several temperatures over the range 130 to 450°K in a specially designed Dewar. The Knight shifts were determined with reference to the ^{27}Al resonance in $AlCl_3$ solution.

3. Results and Discussions

The temperature dependence of the reciprocal magnetic susceptibilities of these compounds is shown in Fig. 1. The experimental data fit a Curie–Weiss law modified by a temperature-independent part, according to

$$\chi = \frac{C}{T - \theta_p} + \chi_0. \tag{1}$$

The numerical values of θ_p and χ_0 are −18K and 81K, 0.71 × 10^{-6} emu/g Oe and 0.50 × 10^{-6} emu/g Oe for $Gd_2Cu_6Al_{11}$ and $Gd_2Co_6Al_{11}$, respectively. The effective magnetic moment values, determined from the Curie constant C, are 7.85 μ_B/Gd atom in $Gd_2Cu_6Al_{11}$ compound and 11.84 μ_B/unit formula in $Gd_2Co_6Al_{11}$. The effective magnetic moment in $Gd_2Cu_6Al_{11}$ is close to that (7.94 μ_B) of the trivalent ion Gd^{3+}, while in $Gd_2Co_6Al_{11}$ the Co atoms' contribution to the effective moment has to be considered.

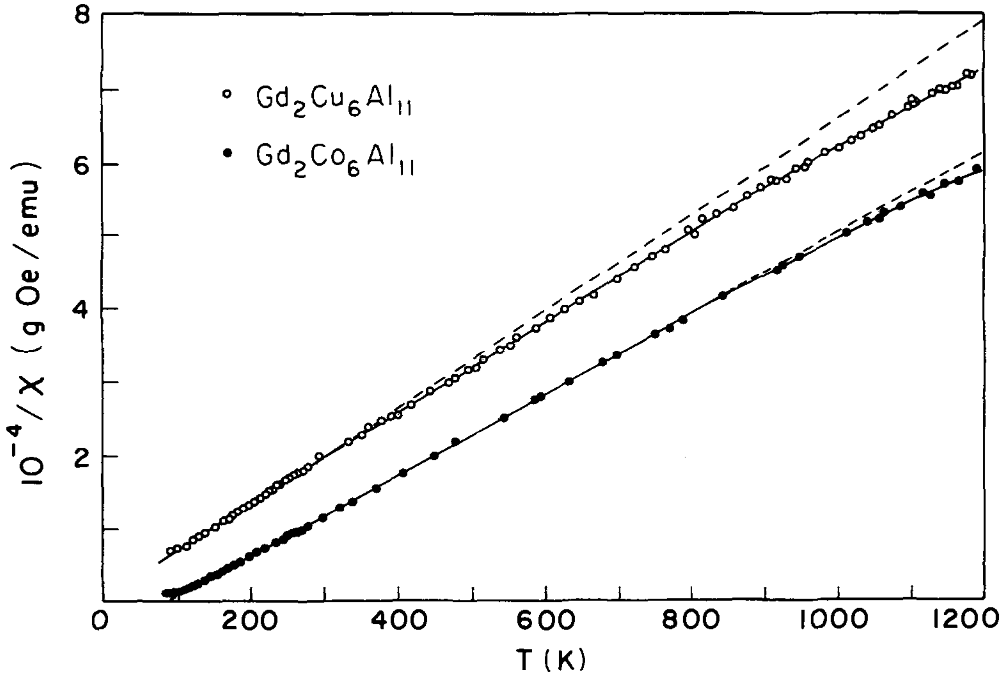

FIG. 1. The reciprocal susceptibility versus temperature for the $Gd_2Cu_6Al_{11}$ and $Gd_2Co_6Al_{11}$ systems.

To separate out the Co contribution to the magnetic susceptibility of $Gd_2Co_6Al_{11}$, we have shown in Fig. 2 the temperature dependence of the Langevin part $(\chi - \chi_0)$ for the $Gd_2Co_6Al_{11}$ and $Gd_2Cu_6Al_{11}$ compounds and the difference between the two curves, which can be considered as the susceptibility contribution from the Co atoms. From this figure it can be seen that $1/\chi$ vs (T) has a linear dependence, indicating paramagnetic behavior. From the slope of $1/\chi$ vs (T) we have determined the effective magnetic moment of Co to be 3 μ_B/atom, which is very close to 3.2 μ_B observed for the pure Co in the paramagnetic state (*4*). This result suggests that the 3*d* electrons of Co atoms are well localized.

It is well known that in the rare earth intermetallic compounds the Knight shift and the susceptibility χ_f of the localized 4*f* electrons, assuming a uniform polarization of the conduction electrons by the 4*f* spins, are linearly related through the expression (*5, 6*)

$$K = K_0 + K'(T) = K_0 + \frac{K_0 \gamma_{sf}(g_f - 1)\chi_f}{2g_f\mu_B^2}, \quad (2)$$

where γ_{sf} is the phenomenological exchange constant, g_f is the 4*f*-electron *g* value, and K_0 is the Knight shift due to the Pauli paramagnetism.

In Fig. 3 the Knight shift for both the compounds is given as functions of the temperature and the susceptibility of the localized 4*f* electrons, $\chi - \chi_0$. Equation (2) is clearly valid (Fig. 3) for the $Gd_2Cu_6Al_{11}$ compound in all ranges of temperature. This is not the case for $Gd_2Co_6Al_{11}$.

From Fig. 3 one can see that the values of the Knight shift in $Gd_2Co_6Al_{11}$ are much smaller than those in $Gd_2Cu_6Al_{11}$ and the

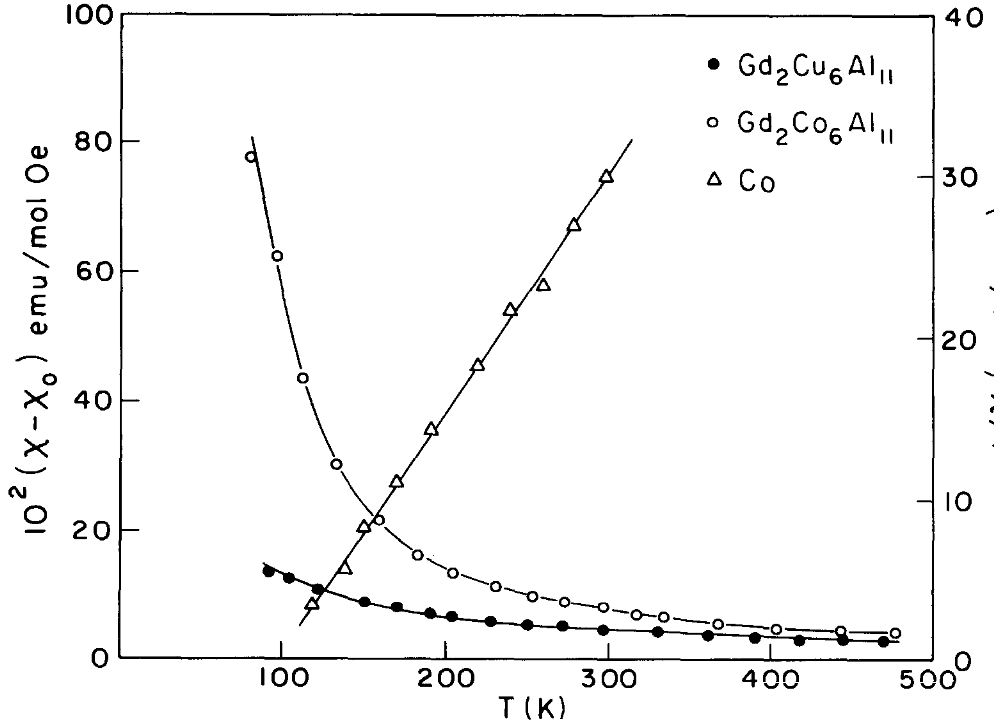

FIG. 2. The temperature dependence of the Langevin magnetic susceptibilities for $Gd_2Cu_6Al_{11}$ (●) and $Gd_2Co_6Al_{11}$ (○) (left ordinate) and of reciprocal susceptibility of Co atoms in $Gd_2Co_6Al_{11}$ compound (△) (right ordinate).

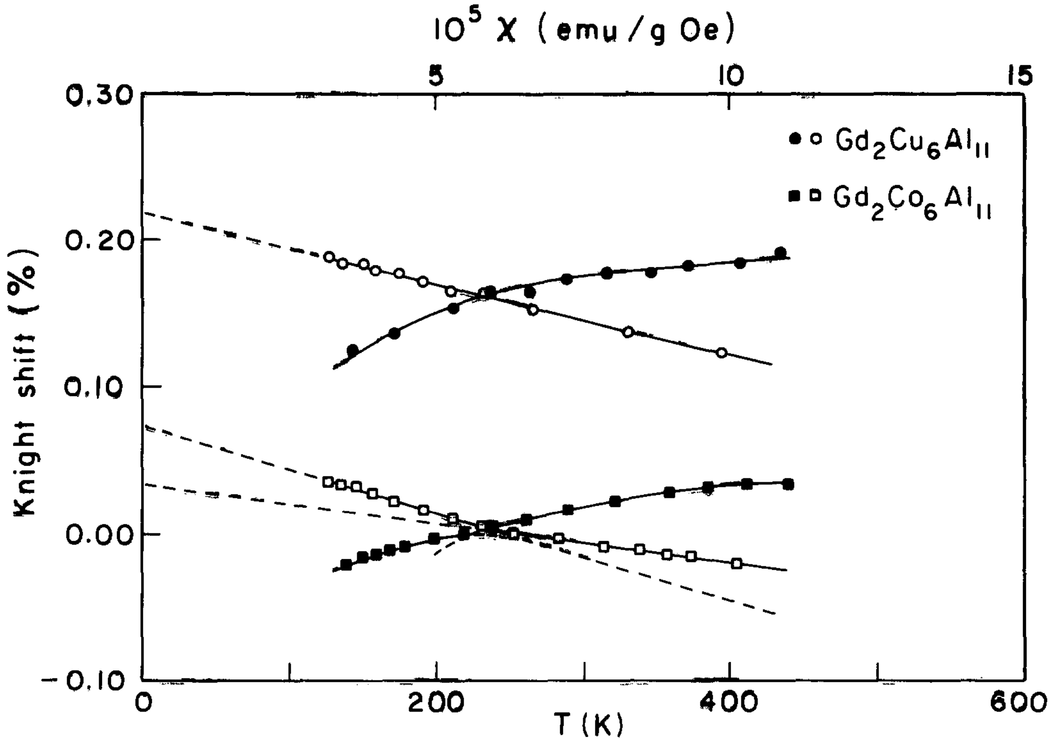

FIG. 3. Curves: the Knight shift of the Al^{27} NMR in Gd$_2$Cu$_6$Al$_{11}$ and Gd$_2$Co$_6$Al$_{11}$ as a function of the temperature (●, ■); straight line: the Knight shift as a function of the 4*f* localized electron susceptibility (○, □).

temperature dependence of the Knight shift for Gd$_2$Co$_6$Al$_{11}$ has a small dip at about 240°K, and at the same temperature $K(\chi_f)$ changes slope. The differences in the values of the Knight shifts and these anomalies can be explained by taking into account the Co atoms' contribution in the Knight shift by an additional negative core polarization term of the form

$$K''(T) = \frac{K_0'' \gamma^1_{sd} \chi_{Co}(T)}{2 g_d \mu_B^2} \qquad (3)$$

and assuming that the Co contribution prevails in the magnetic susceptibility of Gd$_2$Co$_6$Al$_{11}$ in the low-temperature region. Equation (3) refers to the *d* electrons of Co atoms and is analogous to Eq. (2) for $g_d = 2$.

For both the compounds the phenomenological exchange constant γ_{sf} is the same, and from Fig. 3 and Eq. (2) we have obtained the numerical value of $\gamma_{sf} = -1.26 \times 10^{-3}$ eV.

To determine the phenomenological exchange constant γ^1_{sd} between the localized 3*d* electrons of Co atoms and the ns^2 inner shell of Al atoms we have represented in Fig. 4 the Knight shift versus the Co susceptibility as a function of temperature. As was expected, the curve $K(\chi_{Co})$ has an anomaly similar to that in Fig. 3 at about the same temperature. The phenomenological exchange constant $\gamma^1_{sd} = -0.0375$ eV was determined from the slope of the linear part in the low-temperature region, wherein the Co atoms contribution to the magnetic susceptibility prevails (see Fig. 2).

The Co localized magnetic moments have a positive contribution to the bulk Knight shift of the compound Gd$_2$Co$_6$Al$_{11}$, originating with the conduction electrons polarization, of

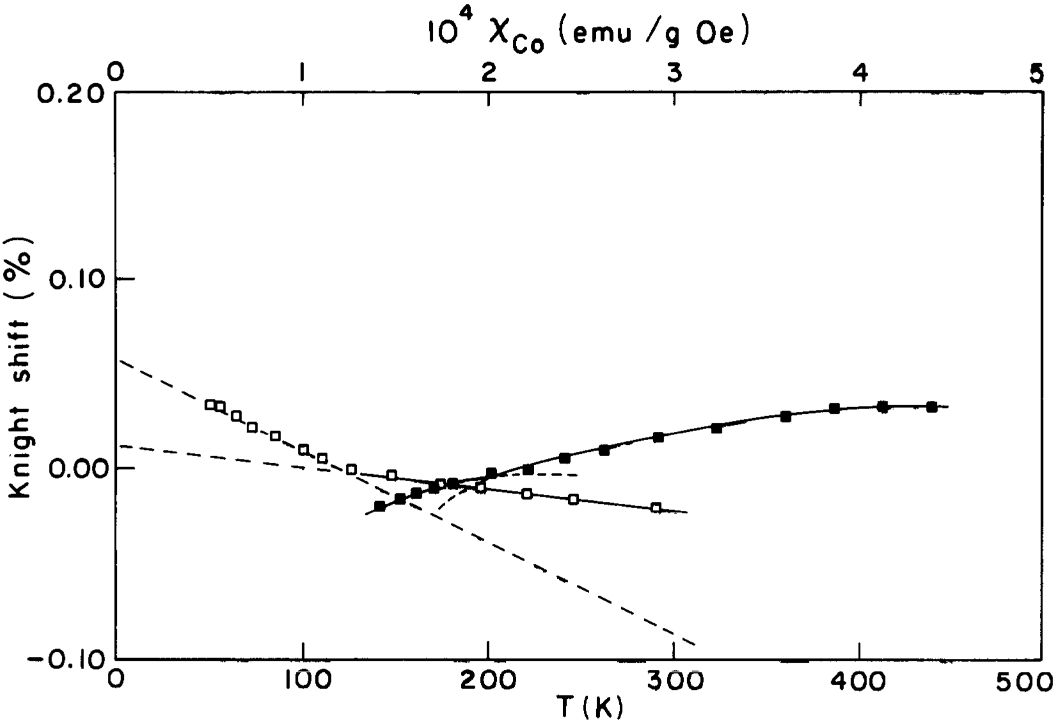

FIG. 4. The Knight shift of the Al^{27} NMR in $Gd_2Co_6Al_{11}$ as a function of the temperature (■) and the Knight shift as a function of the 3*d* localized electron susceptibility of Co atoms (□).

the form

$$K'''(T) = \frac{K_0''' \gamma^{e}_{sd} \chi_{Co}(T)}{2 g_d \mu_B^2}, \quad (4)$$

where γ^{e}_{sd} is the phenomenological exchange constant between the 3*d* localized electrons of Co and the conduction electrons. This new contribution in the bulk Knight shift is reported in Fig. 5 as the difference ΔK between the Knight shifts of $Gd_2Co_6Al_{11}$, which is caused only by Co atoms, versus χ_{Co} in the low-temperature region and as a function of temperature. From this figure one can see the competition between the polarization of the conduction electrons and the core polarization of the Al atoms brought about by the direct overlap of the Co 3*d* orbitals. The temperature dependence of ΔK, as can be seen from Fig. 5, has a concave part in the low-temperature region, corresponding to a more pronounced temperature variation of the conduction electrons polarization than that of the core polarization. From the linear dependence of ΔK versus χ_{Co} (crosses) in the low-temperature region one obtains for the phenomenological exchange constant the value

$$\gamma^{e}_{sd} = 1.33 \times 10^{-3}\,\text{eV}.$$

The bulk Knight shift in the $Gd_2Co_6Al_{11}$ compound may then be described by

$$K(T) = K_0 + \frac{K_0' \gamma_{sf}(g_f - 1)\chi_f(T)}{2 g_f \mu_B^2} + \frac{K_0'' \gamma^{i}_{sd} \chi_{Co}(T)}{2 g_d \mu_B^2} + \frac{K_0''' \gamma^{e}_{sd} \chi_{Co}(T)}{2 g_d \mu_B^2}. \quad (5)$$

The numerical values γ^{i}_{sd} and γ^{e}_{sd} are in good agreement with the results obtained for 3*d*

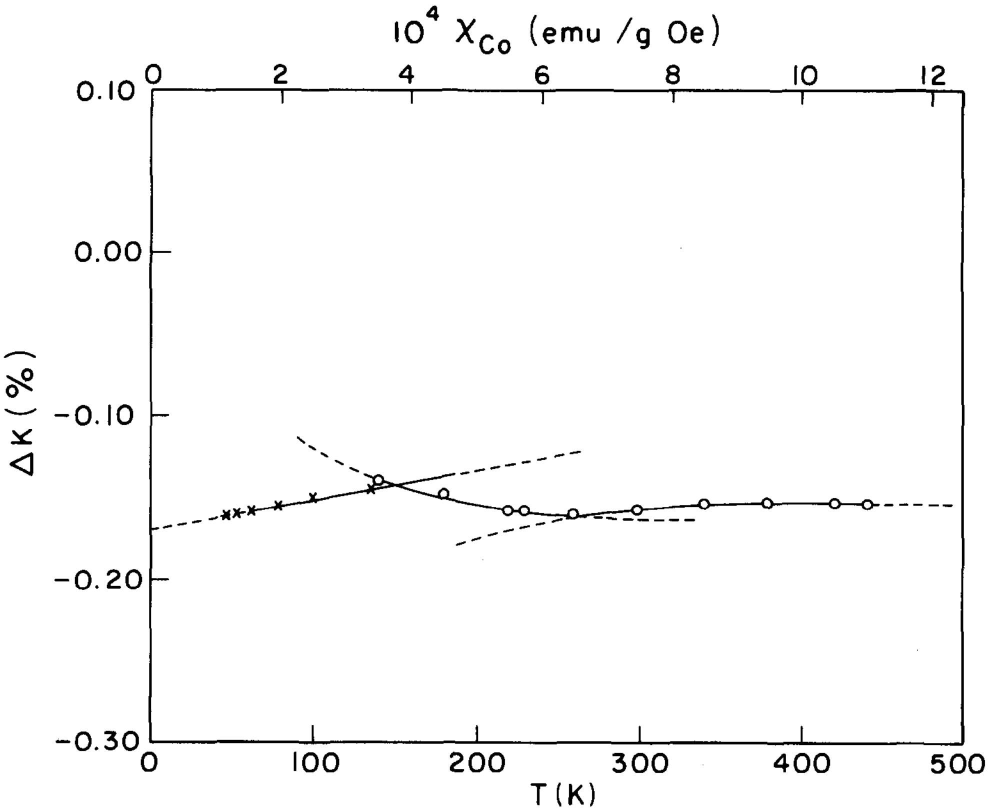

FIG. 5. The contribution in the Knight shift of the Al^{27} NMR in $Gd_2Co_6Al_{11}$ caused by Co atoms as a function of the temperature (○) and of the 3*d* localized electron susceptibility of Co atoms (×).

ferromagnetic metals, which are in the range of 1/10 to 1/100 eV (7).

4. Conclusions

The comparative study of the two alloys $Gd_2Co_6Al_{11}$ and $Gd_2Cu_6Al_{11}$ shows very interesting behavior of the $Gd_2Co_6Al_{11}$ compound. The existence of the two different magnetic elements gives rise to complex exchange interactions, which can be partially separated, by recognizing that in both compounds the Gd atoms have the same contribution. This fact allowed us to use the compound $Gd_2Cu_6Al_{11}$ as a basis for interpreting the more complicated picture of the exchange interactions in the isostructural compound $Gd_2Co_6Al_{11}$.

The analysis has been made using the uniform polarization model which, as is well known, is at best only approximately correct. The oscillatory polarization of the conduction electrons by the localized moments on Gd and Co leads to varying magnetization throughout the crystal. Thus in principle the differing crystallographic type of Al should show different Knight shifts. Actually, only one shift is observed, the mean. Resolution is insufficient to distinguish among the four types of Al present in the material.

The difference in the magnetic susceptibilities of two compounds allows us to determine the Co contribution in the bulk magnetic susceptibility of the $Gd_2Co_6Al_{11}$ compound. An effective magnetic moment of 3 μ_B/Co atom was calculated, which is in good agreement with the value 3.2 μ_B/Co atom for pure Co in the paramagnetic state. A similar approach was used to obtain the Co contribution in the bulk Knight shift of the $Gd_2Co_6Al_{11}$ compound. From this contribution the phenomenological exchange constant γ^e_{sd} between the localized 3*d* electrons of Co atoms and conduction electrons was determined. Because of the position of the Co atoms in the crystalline lattice, the 3*d* orbitals do not overlap with each other, but a superposition between these orbitals and those of the Al atoms can take place. The Co atoms interact, on the one hand, with the conduction electrons in a fashion similar to that of the rare earth atoms (the well-known *RKKY* interaction), but they also produce a core polarization of the inner shells of Al atoms because of direct overlap.

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