MAGNITUDE AND SIGN OF THE CONDUCTION ELECTRON POLARIZATION IN RARE-EARTH METALS

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From nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) measurements on rare-earth intermetallic compounds, we have determined the magnitude and sign of the conduction electron polarization. These results may be interpreted in terms of a negative exchange interaction of ~0.1 ev between the localized f electrons and conduction electrons.

The NMR of Al^{27} in the rare-earth intermetallic compounds having the cubic Laves structure[1] $X\mathrm{Al}_2$ (X = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and as well, U)[2] was investigated as a function of field (8-14 koe) and temperature (4.2° - 300°K) using a Varian NMR spectrometer. The EPR of EuAl_2 and GdAl_2 was studied at 55 kMc/sec between 100° - 300°K.

Large, temperature-dependent, Knight shifts (k) were observed for all of the $4f$ magnetic compounds CeAl_2 through TmAl_2 and for UAl_2. The sign of k_{Al} obeyed the following simple rule: If we denote by $\vec{S}$, $\vec{L}$, and $\vec{J}$ the spin, orbital, and total angular momentum of the ground state of the rare-earth ion, then

$$k_{\mathrm{Al}} > 0 \text{ for } \vec{J} = \vec{L} - \vec{S},$$
$$k_{\mathrm{Al}} < 0 \text{ for } \vec{J} = \vec{L} + \vec{S}. \tag{1}$$

For the nonmagnetic compound LaAl_2, $k_{\mathrm{Al}} = +0.13 \pm 0.02\%$. The Knight shift results from the contact hyperfine interaction $A\vec{I}\cdot\vec{s}$ between the Al^{27} nuclear spin $\vec{I}$ and the s conduction electron spin $\vec{s}$.

An explanation for the magnitude, sign, and temperature dependence of k_{Al} in the magnetic compounds may be found in the enhanced conduction electron polarization that results from the exchange interaction between the localized f electrons and the conduction electrons; i.e.,

$$\mathcal{H}_{\mathrm{ex}} = -\mathcal{J}_{sf}\vec{S}\cdot\vec{s}. \tag{2}$$

By virtue of $\mathcal{J}_{sf}$ an additional hyperfine interaction, $A'\vec{I}\cdot\vec{S}$, exists, which we assume for simplicity to be isotropic. The fact that $\vec{J}$ is a good quantum number necessitates projecting $\vec{S}$ on to $\vec{J}$; hence $A'\vec{I}\cdot\vec{S} \rightarrow A'\vec{I}\cdot\vec{J}\langle\vec{S}\cdot\vec{J}\rangle/J(J+1)$. We may then express the Knight shift at a temperature T,

$$k = k_0\left[1 + \frac{\mathcal{J}_{sf}\chi_f}{g_f g_s n_f \beta^2}\frac{\langle\vec{S}\cdot\vec{J}\rangle}{J(J+1)}\right], \tag{3}$$

where k_0 is the Knight shift in the absence of f-electron polarization effects and χ_f/n_f is the f-electron susceptibility (at T) per rare earth ion.

Since

$$\langle\vec{S}\cdot\vec{J}\rangle < 0 \text{ for } \vec{J} = \vec{L} - \vec{S},$$
$$\langle\vec{S}\cdot\vec{J}\rangle > 0 \text{ for } \vec{J} = \vec{L} + \vec{S}, \tag{4}$$

the observed relations (1) for k are consistent with a negative $\mathcal{J}_{sf}$. The values of $\mathcal{J}_{sf}$ derived from the observed k and measured values[3] of χ using (2) are given in Fig. 1. The value of $k_{\mathrm{Al}}(\mathrm{LaAl}_2)$ was assumed for k_0.

For PrAl_2 the temperature independence of $\mathcal{J}_{sf}$ was established by measurements between 77° and 300°K. Since k_{Al} (PrAl_2:300°K) is but 4 times k_0, it was possible to verify that k is not proportional to χ, as a function of T, but is given by Eq. (3). For all but Ce, Pr, Sm, and Gd, the magnitude and field dependence of the linewidth at 300°K indicated that the Knight shift was anisotropic and could not be accounted for by electronic dipolar broadening. The large linewidths result from either an anisotropic exchange interaction or partial quenching of the orbital angular momentum (anisotropic g) or both.

We briefly mention certain other results of these experiments. Large Al^{27} quadrupole interactions were observed, the magnitudes of which are given in Table I. The La^{139} NMR in LaAl_2 was studied as a function of temperature and k_{La} was found to be weakly temperature dependent (see Table I). The relative broadening of the La^{139} and Al^{27} NMR vs either Gd or Dy impurity concentration in LaAl_2 was studied and found to be consistent with the Ruderman-Kittel-Yosida[4,5] conduction electron polarization description.

Yosida[5] has shown that the conduction electron

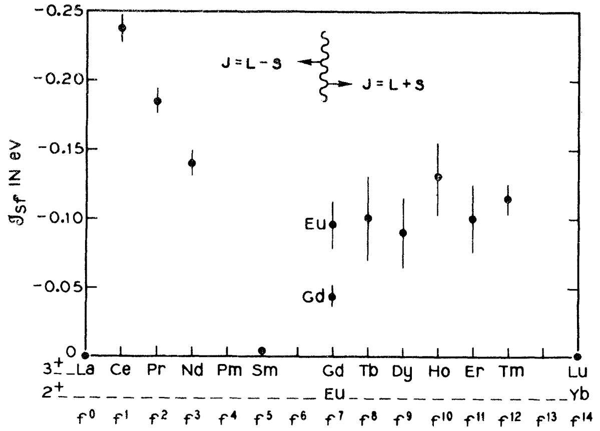

FIG. 1. The magnitude and sign of the exchange interaction in the rare earth-aluminum intermetallic compounds of the cubic Laves structure $X\mathrm{Al}_2$ as determined from the Knight shift of the Al^{27} NMR and the measured susceptibilities. The number of $4f$ electrons and the corresponding valence is that which is usually given for the free ion. [C. Kittel, Introduction to Solid-State Physics (John Wiley & Sons, Inc., New York, 1956).] X-ray data and susceptibility measurements support the assignment given in the figure for these quantities. The relative size of the anisotropic interaction observed is indicated by the vertical line. Neither the inconstancy of $\mathcal{J}_{sf}$ nor its magnitude and sign are understood at present. The anomalously small value of $\mathcal{J}_{sf}(\mathrm{SmAl}_2)$ derived probably results from the assumption that the state ${}^6H_{5/2}$ for the Sm^{3+} ion is pure. Due to the close spacing of the fine structure levels and the importance of crystal field and exchange interactions in admixing states for which $J \neq \frac{5}{2}$, this assumption is questionable.

polarization gives rise to an electronic g shift of the EPR of the magnetic ions in metals. The fractional change in the g value expected is

$$\Delta g/g = 3n\mathcal{J}_{sf}/2n_f g\epsilon_f. \tag{5}$$

Here, $2n/n_f$ is the number of conduction electrons per atom, and ϵ_f is the Fermi energy.

The observed shift $\Delta H = H_{\mathrm{res}} - H_0$ was only a fraction of the half-power linewidth ($\delta H \sim 900$ oe in GdAl_2). The resonance line shows a Lorentz shape as would be expected in the case of strong exchange narrowing.[6] The observed line profile indicated a mixture of the real and imaginary parts of the rf susceptibility.[7] The relative admixture was determined for each measurement. The field for resonance showed a temperature dependence which results from demagnetizing effects.

Table I. The Al^{27} nuclear electric quadrupole interaction constants e^2qQ^{27} as determined from the field dependence of the broadening of the $1/2 \longleftrightarrow -1/2$ transition. The temperature dependence of the Knight shift of the La^{139} NMR in LaAl_2 is given in the lower portion of Table I. No measurable temperature dependence was found for the Al^{27} Knight shift in LaAl_2: $k_{\mathrm{Al}} = 0.13 \pm 0.02\,\%$. (Reference solutions: LaNO_3 and KAlSO_4.)

Compound	Valence	e^2qQ^{27} (Mc/sec)
LaAl_2	3+	4.63
CeAl_2	3+	4.54
PrAl_2	3+	4.54
YbAl_2	2+	2.30
UAl_2	?	4.31

Temp(°K)	4.2	20	295
$k_{\mathrm{La}}(\mathrm{LaAl}_2)$, %	0.65	0.64	0.60

This dependence was eliminated by linear extrapolation to zero magnetization.

Using these procedures, we obtained the values

$$\mathrm{GdAl}_2\text{: } g = 1.982 \pm 0.003, \quad \Delta g = 0.010,$$

$$\mathrm{EuAl}_2\text{: } g = 1.994 \pm 0.003, \quad \Delta g = 0,$$

where Δg is obtained from a comparison with the ionic value for Gd of $g = 1.992$ estimated by Lacroix.[8] A comparison with published measurements on ionic crystals[9] indicates that crystalline field effects on the g value are negligible. The measured $\Delta g/g$ in GdAl_2 leads to a value of $\mathcal{J}_{sf} = -0.03$ ev if we assume $\epsilon_f = 5$ ev and $n/n_f = 1$. No polarization was detected within our accuracy in EuAl_2.

It remains in interpreting the NMR results to justify the statement [Eq. (3)] that the conduction electron polarization at the aluminum sites due to the exchange interaction with the rare earth ions is proportional to $\mathcal{J}_{sf}$ as though the rare earth ion spins imposed a uniform magnetic field on the conduction electrons. In actual fact the s-f interaction is highly localized. Suppose that $\chi(\vec{r} - \vec{r}_i)$ is the conduction electron magnetization at $\vec{r}$ due to a localized "field" of unit strength at $\vec{r}_i$ (in this case the exchange field). Then the total magnetization at $\vec{r}$ is proportional to

$$\sum_{\substack{\text{rare earth}\\ \text{sites } \vec{r}_i}} \chi(\vec{r} - \vec{r}_i) = \sum_{\vec{r}_i, \vec{q}} \chi(\vec{q}) e^{i(\vec{r} - \vec{r}_i)\cdot\vec{q}},$$

where the $\chi(\vec{q})$'s denote the Fourier coefficients in the expansion of χ, assuming the usual boundary conditions. The sum over $\vec{r}_i$ gives zero unless $\vec{q}$ is zero or one of the reciprocal lattice vectors $\vec{K}$. Thus the magnetization is

$$\chi(0)+\sum_{\vec{K}}\chi(\vec{K})e^{i\vec{r}\cdot\vec{K}}.$$

The leading term is, of course, the magnetization due to a spatially uniform field of unit strength. Assuming that χ is simply the Ruderman-Kittel susceptibility, $\chi(\vec{q})$ decreases from $\chi(0)$ to zero at $q=2k_f$. Therefore, unless $2k_f$ is comparable with one of the $\vec{K}$'s the sum will be negligible, and Eq. (3) is justified. The internal consistency of the data suggests that no such special conditions prevail.

Only for a naive model would one expect a detailed agreement between $\mathcal{J}_{sf}$ as derived from the NMR and EPR experiments since the former gives the polarization at the Al site while the latter that at the Gd site. The fact that both measurements show a negative polarization is strong evidence for assuming $\mathcal{J}_{sf}< 0$.

To our knowledge this is the first determination of the sign of conduction electron polarization in a magnetic metal.[10]

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[1] The cubic Laves structure AB_2 belongs to the space group $O_h{}^7=Fd3m$; the point symmetry for the A site is $\bar{4}3m$ and the B site $\bar{3}m$. An axial quadrupole interaction is possible for the B site. All NMR measurements were made above the Curie point.

[2] The compounds were prepared by induction heating of stoichiometric amounts of the pure metals in silica or alumina crucibles in an argon atmosphere. J. H. Wernick and S. Geller, Trans. Am. Inst. Mining, Met. Petrol. Engrs. (to be published). S. E. Haszko, Trans. Am. Inst. Mining, Met. Petrol. Engrs. (to be published). For the NMR and EPR experiments, the samples were pulverized and sieved (400 mesh).

[3] H. J. Williams and R. C. Sherwood (private communication).

[4] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

[5] K. Yosida, Phys. Rev. 106, 893 (1957).

[6] P. W. Anderson and P. R. Weiss, Revs. Modern Phys. 25, 269 (1953). Assuming dipolar broadening, this theory predicts $\delta H=500$ oe in GdAl$_2$.

[7] M. Peter and B. T. Matthias, Phys. Rev. Letters 4, 449 (1960).

[8] R. Lacroix, Helv. Phys. Acta 30, 374 (1957).

[9] J. W. Orton, Reports on Progress in Physics (The Physical Society, London, 1959), Vol. 22, p. 204.

[10] J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids 2, 85 (1957), have found no shift for the EPR of Mn^{++} in copper but have detected a broadening of the Cu NMR.

OPTICAL OBSERVATION OF SPIN-ORBIT INTERACTION IN GERMANIUM

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Philipp and Taft[1] have recently determined the optical constants of germanium from the measurement of reflectivity in a broad wavelength range. In the reflection spectrum they observed near 2 ev a characteristic peak which Phillips[2] from an analysis of the absorption curve ascribed to the transition $L_{3'}\rightarrow L_1$ (see also Roth and Lax[3]). Our measurements of the reflection spectrum on etched single crystals of germanium have shown that this peak is split into two peaks, a at 2.1 ev and b at 2.3 ev (see Fig. 1). Using the optical constants as determined by Philipp and Taft[1] and considering the splitting $a-b$ as a small perturbation of the reflectivity reproduced in reference 1, it is possible to show that in the absorption

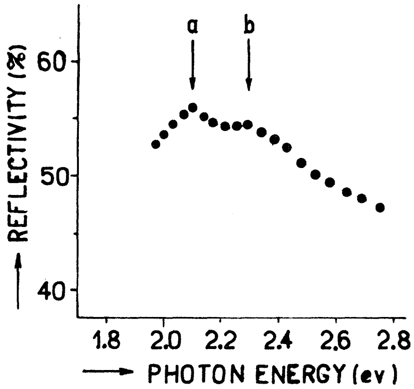

FIG. 1. Reflection spectrum of germanium (at 300°K) near 2 ev.