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Indirect evidence for exchange modification of the conduction bands in $R\mathrm{Al}_2$ compounds

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The self-polarization contribution to the total hyperfine field at a rare-earth nucleus should be directly correlated with a variation in the hyperfine splitting parameter as seen by the $4f$ electron of the rare-earth ion. Comparison of data on the hyperfine field in ordered ErAl_2 and DyAl_2 with paramagnetic resonance results for Er and Dy in ScAl_2, LuAl_2, and YbAl_2 suggests that the self-polarization effect is large in the ferromagnetic phase but negligible in the paramagnetic phase. Analysis of available data on some Pr and Tm compounds also suggests self-polarization effects to be negligible in the paramagnetic phase. We conclude that modification of the conduction-electron band structure due to exchange splitting effects may play an important role in the rare-earth$-\mathrm{Al}_2$ compounds.

In a recent study[1] of the hyperfine field in ordered rare-earth$-\mathrm{Al}_2$ Laves-phase intermetallics we found fields originating from exchange polarization of the conduction bands (self-polarization fields) which were much larger than expected and between 12% and 16% of the overall hyperfine field. The size of these fields and their variation as function of rare-earth ion lead us to conclude that orbital as well as spin polarization of the conduction bands was present and that the former gave rise to large orbital self-polarization fields. A further investigation, this time on Zn compounds[2] (again ordered magnetically), appears to show similar behavior to the Al_2 compounds suggesting that the presence of orbital polarization may be a common feature. These results have prompted us to search for other experiments or results which might support our conclusions about orbital polarization and it is this which we shall discuss in the following.

The hyperfine field associated with the orbital part of electronic character is particularly large[3] so that experiments involving measurement of hyperfine fields are sensitive monitors. At least two experiments other than nuclear magnetic resonance in the ferromagnetic state (as used in the aforementioned experiments) can give information on the "self-polarization" field and one can be used to measure it directly. In the first case, one can measure nuclear magnetic resonance of the rare-earth nucleus in the paramagnetic state as was very well demonstrated by Jones[4] and more recently in pressure-dependent measurements.[5] This technique, akin to nuclear magnetic resonance in the ferromagnetic phase, is essentially limited for relaxation reasons, to singlet-ground-state systems.[5] The second measurement technique, as we shall discuss further, is the technique of electron paramagnetic resonance and at least in metals, this is limited to Kramer's ions (or at least to date). Since both of the experiments referred to are in the paramagnetic phase we shall follow a theoretical approach strictly limited to this. The Hamiltonian for an interacting system of nuclei and conduction electrons in the presence magnetic field has been given by Yosida[6] and for the present discussion we will concentrate only on the term involving nuclear and electronic spins whose energy has the form

$$\Delta E = -\left(\frac{3n}{N}\right)^2 \frac{2\pi}{E_F} A(0) J(0) \times \sum_{m,n} F(2k_F R_{nm}) (\vec{I}_n \cdot \vec{S}_m) \ , \qquad (1)$$

where the sum runs over lattice sites n and m and N is the total number of atoms in the sample. This notation is taken directly from Yosida[6] and the wave-vector independent term is quoted for simplicity. It should be noted that at least two other terms of this type are present; core polarization arising from exchange spin polarization of the d-band electrons and an orbital term from orbital polarization[7] of the conduction band (d character). These may be accounted for in the first instance by using different $F(2k_F R_{nm})$ and by substituting $\vec{J}_m$ for $\vec{S}_m$. For the case of $n \neq m$

TABLE I. Self-polarization field as a percentage of the "ionic" part for Er and Dy in various Al_2 compounds. R infers pure $ErAl_2$ or $DyAl_2$. Data for $ErAl_2$ and $DyAl_2$ are from Ref. 1, the remainder are from Ref. 11.

Ion/host	RAl_2	$ScAl_2$	$YbAl_2$	$LuAl_2$
Er	17 ± 4	0.8 ± 1.2	0.5 ± 1.9	0.1 ± 1.5
Dy	12 ± 5	0.2 ± 0.8	0.2 ± 0.8	2 ± 6

one obtains the transferred hyperfine field at the n site

$$H_T=\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_F}\frac{A(0)J(0)}{g_n\beta_n}\times\sum_{m\neq n}F(2k_FR_{nm})\langle J_z\rangle_m\ , \qquad (2)$$

where we implicitly add the different contributions from different $A(0)$'s etc. For $n=m$ we obtain the self-polarization field, $H_{\rm sp}$ (at a single site)

$$H_{\rm sp}=\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_F}\frac{A(0)J(0)}{g_n\beta_n}\langle J_z\rangle\ . \qquad (3)$$

The two fields expressed by Eqs. (2) and (3) should be measurable in a nuclear magnetic resonance experiment. If we now consider the fields seen by the electron rather than the nucleus we have for the electron energy (including Zeeman and direct hyperfine interactions)

$$E=g_J\mu_BHJ_z+A\langle I_z\rangle J_z-\left(\frac{3n}{N}\right)^2\frac{2\pi}{E_F}A(0)J(0)\langle I_z\rangle J_z\ , \qquad (4)$$

where μ_B is positive and we have ignored the g shift term.[6] This can consequently be rewritten

$$E=g_J\mu_BHJ_z+(A+\Delta A)\langle I_z\rangle J_z \qquad (5)$$

(we have ignored transferred hyperfine field terms). The variation in the hyperfine parameter over the ionic value[8] has been referred to by various authors[9,10] studying EPR in metals but it appears to have been neglected that this term is simply the "self-polarization" term from NMR [Eq. (3)]. There should thus be a one to one correspondence between the $\Delta A/A$ determined from EPR and that found from NMR. In Table I we compare the results of EPR and NMR measurements on Laves-phase Al_2 compounds. Since one cannot measure EPR in concentrated rare-earth systems, dilute alloy results are used[11] for Er and Dy in $LuAl_2$, $ScAl_2$, and $YbAl_2$ (nonmagnetic). It is clear from this table that the very large variations in ΔA found in the concentrated ferromagnetic phase are not found in the paramagnetic regime. In fact, a survey of available data on EPR in metals[12] indicates that in no dilute metallic system have large deviations in A ever been found.

Since the EPR results show no evidence for the strong polarization found from the NMR[1] we have looked for other data. Jones[4] has studied in detail

TABLE II. Percentage of the self-polarization and transferred hyperfine field with respect to the ionic field taken from paramagnetic-phase NMR data (Ref. 4).

Compound		Knight shift Experiment	Ionic	Percentage difference (Experiment-ionic/ionic)
PrP	4 K	6.4 ± 0.1	5.8	10 ± 1
	30 K	6.3 ± 0.1	5.7	10 ± 1
TmP	4 K	77 ± 1	79	−2.5 ± 1.3
	20 K	41 ± 1	41	0 ± 2.4
PrAs	1.4 K	6.5 ± 0.1	5.8	12 ± 2
	27 K	6.4 ± 0.1	5.7	12 ± 2
TmAs	1.4 K	71 ± 1	72	−1.4 ± 1.4
	27 K	38 ± 0.5	41	−7.3 ± 1.2
TmSb	1.4 K	89 ± 1	87	2.3 ± 1.1

the nuclear magnetic resonance of Pr and Tm in various pnictide and chalcogenide compounds in the paramagnetic phase. The ionic part of the hyperfine field ($A\langle J_z\rangle$) can be calculated directly since the susceptibility in these compounds has been measured.[13] The results are given in Table II together with the percentage difference here representing the sum of self-polarization and transferred hyperfine fields. In the majority of cases one observes small differences ($\leq 2.5\%$) between the predicted ionic hyperfine field and the measured value. Two exceptions seem to be PrP and PrAs but these do seem to be exceptions rather than the rule. Using EPR g-shift data we have tried to estimate the transferred hyperfine fields Eq. (2) but these are in all cases at most 5% of the total hyperfine field and coult not, therefore, explain the PrP and PrAs results.

We believe that the comparison of hyperfine field data on the $R\mathrm{Al}_2$ compounds in the paramagnetic and ferromagnetic phases suggests that the strong polarization observed in the ferromagnetic domain does not persist into the paramagnetic region. It remains to suggest how this comes about. From Eq. (4) it is assumed that as one goes from paramagnetic to ferromagnetic phase the constants $A(0)$, $J(0)$, etc., remain constant and that the magnetization of the conduction band follows a simple model (free-electron-like bands). Since one does not expect $A(0)$ or $J(0)$ to differ substantially between the ordered and disordered phases one must look to the validity of the free-electron band picture. In these compounds the d bands lie close to the Fermi level[14] and the exchange energy of the localized $4f$ electrons with the band electrons is non-negligible when compared with the width of the predominate band ($5d$) so that some modification of the density of states at the Fermi level would be expected in the ordered phase. Since the density of states would be modified due to exchange splitting, the assumption of linear dependence of band magnetization on the exchange field, from which Eqs. (1)–(4) are derived, would be invalid. One thus concludes that, at least for the $R\mathrm{Al}_2$ compounds, the difference in self-polarization field between the paramagnetic and ferromagnetic phases may derive from exchange splitting of the conduction bands in the ferromagnetic phase. A similar argument has been used[15] to explain crystal-field parameter sign changes between the paramagnetic and ferromagnetic phases.

From the results presented in Table I we have concluded that the self-polarization field increases in the ferromagnetic phase. More measurements on other $R\mathrm{Al}_2$ compounds in the paramagnetic phase would be desirable but difficult since by EPR only the Kramer's ions Ce, Nd, Er, Dy, and Yb are generally seen and in this case, at least one (YbAl_2) is nonmagnetic. CeAl_2 shows anomalous properties[16] leaving only NdAl_2 where one might hope to measure the self-polarization effect. The results presented in Table II cannot be used as conclusive evidence for the lack of significant self-polarization effects in the paramagnetic phase because of the large effects found for PrP and PrAs. We therefore believe that more measurements should be made, possibly on dilute zinc compounds, to see whether or not the band-structure modification effect is "universal" or to see under what conditions it becomes important. Ideally some form of experiment enabling direct measurement of the density-of-states curve through the ordering transition would be desirable.

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