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Comments

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Pressure dependence of the hyperfine field in Eu intermetallics

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Recent measurements of the pressure dependence of the hyperfine field at the Eu nucleus in Eu intermetallic compounds have been interpreted by terms of volume dependence of the transferred field and variations of the local-moment–conduction-electron exchange parameters. It is suggested that an alternative solution may be the pressure dependence of number *d* electrons at the rare-earth site and its influence upon the self-polarization field. A test of the validity of the latter hypothesis is suggested.

In a recent paper,[1] Abd-Elmeguid *et al.* reported the results of measurement of the Mössbauer effect in several Eu intermetallic compounds under pressure. Their hyperfine field data for the Eu nuclei show that in all but two cases ($EuZn_2$ and $EuPt_2$) the total hyperfine field becomes increasingly more negative with increasing pressure. It is generally assumed that the total field can be written as the sum of three terms, viz,

$$B_{\mathrm{eff}} = B_{4f} + B_{\mathrm{sp}} + B_{\mathrm{NN}} \quad , \tag{1}$$

where dipolar fields are ignored. B_{4f} is the field arising from the $4f$ electrons,[2] B_{sp} is the self-polarization field (due to polarization of the conduction electrons local to the ion by $4f$-conduction-electron exchange) and B_{NN} is the field felt by the nucleus due to conduction electron polarization transferred from neighboring sites where local-moment–conduction-electron exchange occurs. Since for Eu^{2+} in the compounds considered the local moment is saturated at $\frac{7}{2}$ we can approximate $\partial B_{4f}/\partial p$ to zero. B_{sp} is found in all cases to be greater than zero and reasoning that it is primarily due to *s* electrons, Abd-Elmeguid *et al.*[1] assume that $\partial B_{\mathrm{sp}}/\partial p > 0$ so it cannot be the origin of the observed negative pressure dependence of B_{eff}. By deduction the observation of $\partial B_{\mathrm{eff}}/\partial p < 0$ must arise due to $\partial B_{\mathrm{NN}}/\partial p$ being less than zero.

The hyperfine fields, B_{sp} and B_{NN}, arise from polarization of the conduction-band electrons due to exchange with the various magnetic localized moments. In its most general form the spatial variation of the conduction-electron polarization $[\vec{\sigma}(\vec{r})]$ can be written:

$$\vec{\sigma}(\vec{r}) = \sum_{\alpha,n} \frac{J_n}{g^2 \mu_B^2 V} \times \sum_q \chi_n(\vec{q}) \exp[i\vec{q}\cdot(\vec{R}_\alpha - \vec{r})] \vec{S}(\vec{R}_\alpha) \quad , \tag{2}$$

where the α sum is over all sites of magnetic moments at which exchange occurs and n is used to denote the band concerned (e.g., *s,p,d*).

Considering some ion as an origin we have the polarization locally

$$\vec{\sigma}(0) = \sum_{\alpha,n} \frac{J_n}{g^2 \mu_B^2 V} \sum_q \chi_n(\vec{q}) e^{i\vec{q}\cdot\vec{R}_\alpha} \vec{S}(\vec{R}_\alpha) \quad . \tag{3}$$

The hyperfine field produced by this polarization is written as

$$B = \sum_n \tilde{A}_n \langle \sigma_n(0) \rangle \quad . \tag{4}$$

This field is actually composed [from Eq. (3)] of *both* B_{sp} and B_{NN}. We obtain B_{sp} by taking the first term in the sum $(\alpha = 0)$,

$$B_{\mathrm{sp}} = \sum_n \tilde{A}_n \frac{J_n}{g^2 \mu_B^2} \chi_n(0) \langle S(0) \rangle \quad . \tag{5}$$

B_{NN} is given by the remaining terms in the sum $(\alpha > 0)$. As is well known, a simplified form of Eq. (3) for the sum over ions not at the origin is obtained if one assumes the conduction electrons are free electrons—this is the Ruderman-Kittel-Kasuya-Yosida (RKKY) formula. From Eq. (5) we see that B_{sp} is proportional to the product $\rho_n(E_F) J_n$ where $\rho_n(E_F)$ is the partial density of states at the Fermi level. The asymptotic solution of the RKKY form of the polarization produced by distant magnetic neighbors also leads to the conclusion that

$$B_{\rm NN} \propto J_n \rho_n(E_F) f(k_F r) \ , \qquad (6)$$

where the function $f(k_F r)$ is some spacial function which may not be as simple as the straightforward RKKY form. Assuming the RKKY form of $f(k_F r)$, the spatial sum does not change with volume so that one would expect the pressure dependence of $B_{\rm sp}$ and $B_{\rm NN}$ to arise from pressure dependence of the same quantities, i.e., J_n and $\rho_n(E_F)$. It is not, therefore, consistent to ignore the pressure dependencies of $B_{\rm sp}$ and take account of that of $B_{\rm NN}$.

From Eqs. (4) and (5), taking only s and d electrons we see that

$$B_{\rm sp} = \tilde{A}_s \langle \sigma_s(0) \rangle + \tilde{A}_d \langle \sigma_d(0) \rangle \qquad (7)$$

and the s term is positive[3] whilst the d term is negative (assuming J_s and J_d both >0). Positive values found in all cases for $B_{\rm sp}$ then suggest dominance (though not of what absolute value) of the s term. The transferred hyperfine fields are in all cases bar $\rm EuZn_2$ and $\rm EuPt_2$ found to be negative. To explain the observed ferromagnetic ordering temperatures the RKKY functions $[f(k_F r)$ in Eq. (6)] must be negative[4] so that a negative value of $B_{\rm NN}$ would again suggest dominance of the s contribution. The cases of $\rm EuZn_2$ and $\rm EuPt_2$ may indicate the presence of d effects in the transferred hyperfine field. In terms of the pressure dependence of $B_{\rm sp}$ and $B_{\rm NN}$, since we expect them both to depend upon the same pressure-dependent quantities [the products $\rho_n(E_F)J_n$] it seems reasonable in the most simple-minded model to assume the fractional changes in $B_{\rm sp}$ and $B_{\rm NN}$ to be the same, i.e.,

$$\frac{\partial B_{\rm sp}/\partial p}{B_{\rm sp}} = \frac{\partial B_{\rm NN}/\partial p}{B_{\rm NN}} \ .$$

In this case, since in all the compounds measured by Abd-Elmeguid *et al.*[1] $|B_{\rm sp}| > |B_{\rm NN}|$, the dominant pressure effect should come from change in $B_{\rm sp}$ with pressure.

We must therefore explain how one arrives at $B_{\rm sp} > 0$ but $\partial B_{\rm sp}/\partial p < 0$ if one wishes to reconcile the experimental results with our "theoretical" understanding.

We believe a plausible explanation for the pressure dependencies may be found. Let us first assume, following the previous reasoning, that pressure dependence of $B_{\rm sp}$ is of prime importance in $\partial B_{\rm eff}/\partial p$. We rewrite Eq. (7) as

$$B_{\rm sp} = K_s \rho_s(E_F) + K_d \rho_d(E_F) \ ,$$

where K_s and K_d engulf the relevant exchange constants, hyperfine parameters, etc., and we recall that $K_s > 0$ and $K_d < 0$. Noting that to first order K_s and K_d do not depend upon pressure,[5]

$$\frac{\partial B_{\rm sp}}{\partial p} = K_s \frac{\partial \rho_s(E_F)}{\partial p} + K_d \frac{\partial \rho_d(E_F)}{\partial p} \ . \qquad (8)$$

In a free-electron model $\rho_s(E_F) \propto 1/a$ where a is the lattice parameter so

$$\frac{\partial \rho_s(E_F)/\partial p}{\rho_s(E_F)} \simeq \frac{\partial a/\partial p}{a} \simeq -\frac{\kappa}{3} \ ,$$

where κ is the compressibility. From the results of Ref. 1 this gives $\partial \rho_s(E_F)/\partial p/\rho_s(E_F) \simeq 3.3 \times 10^{-4}$/kbar. If the s contribution dominated totally in Eq. (8) then

$$\frac{\partial B_{\rm eff}}{\partial p} \simeq \frac{\partial B_{\rm sp}}{\partial p} \simeq B_{\rm sp} \left(\frac{\partial \rho_s(E_F)/\partial p}{\rho_s(E_F)} \right) \ .$$

Using the value of κ from Table I of Ref. 1 this would give a maximum value due to s-density variation of the order of 4×10^{-3} T/kbar, well below the experimental values and of opposite sign.

For the d electrons, if the d band simply broadens maintaining the number of d electrons constant then the negative d contribution to $B_{\rm sp}$ will decrease making $B_{\rm sp}$ (and hence $B_{\rm eff}$) more positive. However, let us write

$$\frac{\partial B_{\rm sp}}{\partial p} = K_d \frac{\partial \rho_d(E_F)}{\partial p} \simeq K_d \left(\frac{\partial \rho_d(E_F)}{\partial E_F} \frac{\partial E_F}{\partial p} \right) \ . \qquad (9)$$

Duthie and Pettifor[6] have calculated the influence of volume (i.e., pressure) on the Fermi energy and s and d band occupancies in La and Lu. They find that the Fermi energy rises relatively rapidly with decreasing volume (increasing pressure). From their curve of E_F vs V/V_0 (volume over equilibrium volume), near $V/V_0 \simeq 1$ we estimate typically $\partial E_F/\partial(V/V_0) \simeq -0.3$ Ry which leads to $\partial E_F/\partial p \simeq \kappa$ Ry/kbar. Again using compressibility values from Ref. 1 we obtain $\partial E_F/\partial p \simeq 3 \times 10^{-4}$ Ry/kbar. In order to obtain a value for $\partial \rho_d(E_F)/\partial E_F$, band-structure calculations are needed. From results quoted in Ref. 1 for $\rm LaSn_3$, the slope of the $5d$ density of states with energy at the Fermi energy with energy is of the order of 100 (states/Ry)/Ry. Hence $\partial \rho_d(E_F)/\partial p \simeq 3 \times 10^{-2}$ (states/Ry)/kbar. We cannot estimate the absolute change in $B_{\rm sp}$ with pressure due to the d electrons since we do not know all of the parameters in K_d. However, the fractional change in the d contribution is approximately $[\partial \rho_d(E_F)/\partial p]/\rho_d(E_F)$. Again using $\rm LaSn_3$ results, $\rho_d(E_F) \simeq 6$ states/Ry so the fractional change in the d contribution is of the order of 5×10^{-3}/kbar. Can we estimate the d contribution to $B_{\rm sp}$? We know[3] that the $\tilde{A}$'s appearing in Eq. (7) are such that $\tilde{A}_{6s} \simeq -10\tilde{A}_{5d}$. We also know from band-structure results[7] on $\rm LaAl_2$ that typically $\rho_d(E_F) \simeq 8\rho_s(E_F)$ at the rare-earth site. If the $4f$

electron–conduction-electron exchange parameters are essentially equal for s and d bands then the s and d contributions to B_{sp} must be comparable. Since $B_{\text{sp}} > 0$, clearly the s contribution must be slightly larger than that (of opposite sign) from the d's. *As an order of magnitude* let us suppose the s contribution to B_{sp} is typically 16 T and that from the d electrons, −6 T. We calculated the fractional variational d variation to be 5×10^{-3}/kbar so we estimate typically

$$\frac{\partial B_{\text{eff}}}{\partial p} \simeq \frac{\partial B_{\text{sp}}(d \text{ part})}{\partial p} \simeq -3 \times 10^{-2}\ \text{T/kbar} \ .$$

This figure calculated on the basis of typical values for lanthanide compounds is of the correct sign and order of magnitude for most of the compounds studied by Abd-Elmeguid *et al.*[1] What of the exceptions EuZn_2 and EuPt_2 where the opposite sign of $\partial B_{\text{eff}}/\partial p$ is found? The sign of the estimated d contribution to B_{sp} depends upon the sign of $\partial \rho_d(E_F)/\partial E_F$. For LaSn_3 and LaAl_2 it is known that it is positive. Band-structure calculations for EuZn_2 and EuPt_2 are not presently available but if $\partial \rho_d(E_F)/\partial E_F$ is negative (as is possible if E_F is on the other side of a peak in the d density of states) then one can easily reconcile the opposite sign of $\partial B_{\text{eff}}/\partial p$ for these compounds.

In conclusion, it seems that the pressure dependence of the Fermi level coupled with d-band occupancy at the rare-earth site could explain the observed hyperfine results in Eu compounds. In any event, the magnitude of the effect we have estimated on the basis of physically reasonable numbers for Lanthanide compounds suggests that it should be taken into account.

A test may be possible for the previous hypothesis. We have suggested that the d effects dominate the s under pressure. It would be instructive to measure the pressure dependence of the ^{139}La Knight shift in LaAl_2 or LaSn_3. Although the d contribution is supposed[8] to be small in this case, the relative magnitudes of $\partial \rho_s/\partial p$ and $\partial \rho_d/\partial p$ are such that the d term should dominate and the pressure dependence of the Knight shift should consequently be negative.

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