Comments and Addenda

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Comment on the Gd crystalline field and the Gd-Pr exchange in the Van Vleck monopnictides

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(Received 19 September 1977; revised manuscript received 11 October 1978)

We report on the observation of resolved fine structure in the ESR of Gd in PrSb, TmSb, and PrBi single crystals. The fourth-order crystalline-field parameter b_4 was found to increase with the lattice constant upon going from the antimonides to the bismuthides, consistent with the variation of b_4 in the analogous nonmagnetic pnictides. A correlation between b_4 and the Korringa rate in the analogous nonmagnetic compounds suggests that the variation of b_4 is associated with conduction-electron effects. Also the variation of the Gd-Pr exchange parameter, $J_{\text{Gd-Pr}}$ across the pnictides is attributed to variation of the conduction-electron d-d overlap. The data enable us to estimate the pressure derivative of b_4 and $J_{\text{Gd-Pr}}$.

We report an electron-spin-resonance (ESR) study of Gd in the Van Vleck metallic compounds PrSb, PrBi, and TmSb single crystals. The ESR spectra could be interpreted assuming isotropic exchange interaction, $J_{\text{Gd-RE}}$, between the Gd and the host rare-earth ions as well as crystalline field appropriate to Gd^{3+} ion in cubic environment. We found the fourth-order crystalline-field parameter b_4 to increase upon going from the antimonides to the bismuthides, i.e., to increase with the increase of the lattice constant. This is consistent with previous observations in the analogous diamagnetic pnictides.[1,2] Using our data as well as those of others[2,3] we were able to demonstrate the existence of a correlation between b_4 and the Korringa relaxation rate as measured in the same hosts.[3] Such a correlation suggests that the variation of b_4 is probably due to conduction-electron effects. Also the variation of $|J_{\text{Gd-RE}}|$ (increases with the increase of the lattice constant) could be correlated with the Korringa relaxation rate in the analogous nonmagnetic hosts. We argue that this indicates that $J_{\text{Gd-RE}}$ is mediated via conduction electrons (probably of d character). Thus our study clarifies to some extent the origin of the Gd exchange parameter and the crystalline field in metallic Van Vleck pnictides. We believe that it also shed some light on the hard to understand problem of the crystalline field of the host rare-earth ions in the pnictides. The host crystalline field in the Van Vleck pnictides has been a subject of controversy in the past several years.[4-7]

The measurements on PrBi:Gd (1000 ppm), PrSb:Gd (1000 ppm, 800 ppm) and TmSb:Gd (800 ppm) single crystals were carried out at X-band frequency in the helium temperature range. The ESR spectra are characterized by several lines which exhibit angular variation but are largely shifted with respect to the Gd^{3+} free ionic g value ($g=2$). The angular variation of these lines for crystals rotating in the (110) plane are shown in Figs. 1 and 2 for PrBi:Gd and PrSb:Gd, respectively. Similar angular variation have been observed for TmSb:Gd (not shown here). A typical ESR spectrum is shown in Fig. 3. The data were analyzed using the following spin Hamiltonian:

$$\mathcal{H}=g\mu_B\vec{H}\cdot\vec{S}_{\text{Gd}}+\sum_{\text{RE}} J_{\text{Gd-RE}}\vec{S}_{\text{RE}}\cdot\vec{S}_{\text{Gd}} + \left(\frac{1}{60}\right) b_4(O_4^0+5O_4^0), \quad (1)$$

where the first term is the Zeeman interaction, the second term is the exchange interaction between the Gd impurity and the host rare-earth ion, and the last term is the cubic-crystalline-field Hamiltonian with O_4^0 and O_4^4 as spin operators of the fourth degree. We have assumed in our analysis

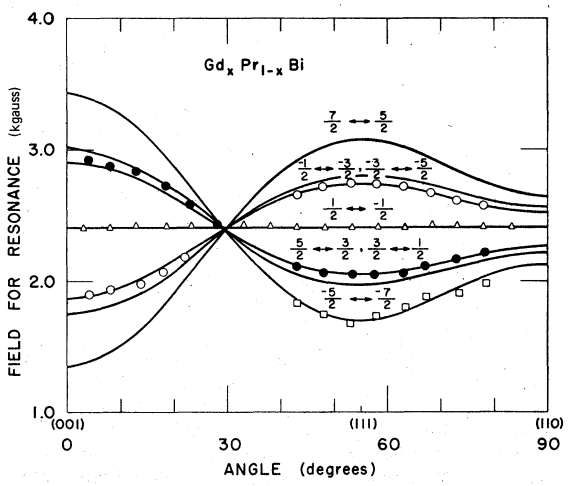

FIG. 1. Angular dependence of the various fine-structure lines of Gd (1200 ppm) in PrBi. The solid lines represent the best fit of the theory [Eqs. (2) and (3)] to the experimental data. This fit yields $b_4 = 47$ G, for Gd in PrBi. As seen the transitions $-\frac{1}{2} \leftrightarrow -\frac{3}{2} \leftrightarrow -\frac{5}{2}$ and $\frac{5}{2} \leftrightarrow \frac{3}{2} \leftrightarrow \frac{1}{2}$ always appear as overlapping lines in our spectra. The measurements were performed at frequency of 9.063 GHz.

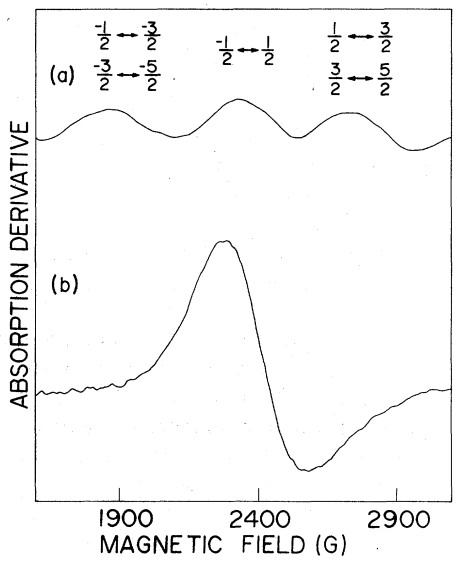

FIG. 3. *ESR* spectra of PrBi:Gd at $T = 1.6$ K (a) represents the [001] direction (b) represents 30° from the [001] direction in the (110) plane.

that $J_{\text{Gd-RE}}$ is isotropic. This is consistent with the isotropic exchange previously found for Er^{3+} in the same hosts. We have neglected also the conduction electron-localized moment exchange interaction as previous studies in the analogous non magnetic pnictide have shown that the effect of this interaction on the line position (field for resonance) can be neglected.[3] Also the sixth-order terms in the cubic-crystalline-field Hamiltonian are small and can be ignored. It is easy to demonstrate that under the above assumptions the field for resonance of the seven transitions with $\Delta m = \pm 1$ can be derived from (1) to be

$$
\begin{aligned}
H(\pm\tfrac{7}{2} \rightleftarrows \pm\tfrac{5}{2}) &= H' \pm 20(1 - 5\phi)b_4, \\
H(\pm\tfrac{5}{2} \rightleftarrows \pm\tfrac{3}{2}) &= H' \pm 10(1 - 5\phi)b_4, \\
H(\pm\tfrac{3}{2} \rightleftarrows \pm\tfrac{1}{2}) &= H' \pm 12(1 - 5\phi)b_4, \\
H(+\tfrac{1}{2} \rightleftarrows -\tfrac{1}{2}) &= H',
\end{aligned}
\tag{2}
$$

where

$$
H' = H_0\{1 + g[(g_J - 1)/g_J](\chi_{VV}/g\mu_B^2 N_0)J_{\text{Gd-RE}}\}, \tag{3}
$$

$$
\phi = l^2m^2 + m^2n^2 + n^2l^2. \tag{4}
$$

Here H_0 is the external field, g_J is the Landé g factor of the host rare-earth ions, μ_B is the Bohr magneton, and χ_{VV} is the host Van Vleck susceptibility. l, m, and n are the direction cosines between the external magnetic field and the cubic axis of the crystal, and N_0 the Avogadro's number.

We identify the observed lines in our spectra (Fig. 3) as the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$, $\frac{5}{2} \leftrightarrow \frac{3}{2} \leftrightarrow \frac{1}{2}$, and $-\frac{5}{2} \leftrightarrow -\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions. The latter transitions always appear as overlapping lines in Figs. 1 and 2 are theoretical fits of (2) to the experimental data. This fit yields the fourth-order crystalline-field parameters b_4(PrBi:Gd) $= 47 \pm 4$ G, b_4(PrSb:Gd)

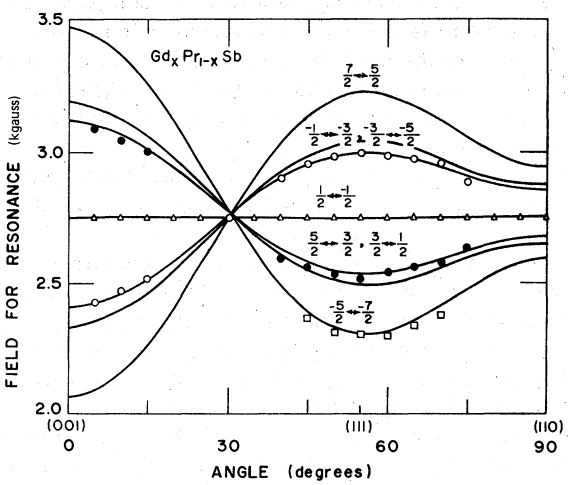

FIG. 2. Angular dependence of the various fine-structure lines of Gd (1000 *ppm*) in PrSb. The solid lines represent the best fit of the theory [Eqs. (2) and (3)] to the experimental data. This fit yields $b_4 = 31$ G for Gd in PrSb. As seen the transitions $-\frac{1}{2} \leftrightarrow -\frac{3}{2} \leftrightarrow -\frac{5}{2}$ and $\frac{5}{2} \leftrightarrow \frac{3}{2} \leftrightarrow \frac{1}{2}$ appear as overlapping lines in our spectra. The measurements were performed at frequency of 9.065 GHz.

$= 31 \pm 3$ G, and b_4(TmSb:Gd) $= 32 \pm 2$ G. The value of b_4 for PrSb:Gd is consistent with that found previously.[8] The error bar, however, is much smaller because of the much better resolution of our ESR spectra. The values of $J_{\text{Gd-RE}}$ are consistent with those reported by Rettori *et al.* and Sugawara *et al.*[9] using mostly powdered samples. In Fig. 4 we have plotted the values of b_4 as a function of the lattice constant for the Van Vleck pnictides as well as for the analogous non-magnetic pnictides measured previously.[1,2] As is clearly seen the values of b_4 for the latter compounds tend to accumulate around two curves corresponding to La compounds and Y compounds respectively. Our data for the Van Vleck compounds are consistent with this behavior: The Pr compounds have lattice constant closer to the La compounds while the Tm compounds have lattice constant closer to those of the Y compounds. Indeed, as is seen in Fig. 4 the values of b_4 for PrSb:Gd and PrBi:Gd are almost sitting on the La curve while b_4 for TmSb:Gd is almost sitting on the Y curve. The main feature of Fig. 4, however, is the increase of b_4 (for each of the series of compounds mentioned above) with the increase of the lattice constant.

The fourth-order crystalline-field parameter b_4 is believed to be associated with the admixture of the excited crystalline field splitted configuration state into the ground S state via the spin-orbit coupling.[1] As such b_4 contains terms proportional to the fourth order crystalline field parameter B_4 originating with the ligands. In the frame of the point-charge model (PCM) B_4 is expected to be inversely proportional to the fifth power of the lattice constant.[4] Thus, the increase of b_4 with lattice constant in Fig. 4 indicates the failure of the point charge model. This is in agreement with Knight shift under pressure by Weaver and Schirber[5] and a very recent neutron scattering under pressure by Vettier *et al.*[7] These studies have shown that the PCM fails to predict the pressure dependence of the crystalline field levels of the host rare earth ions in the Van Vleck pnictides. The Knight shift study also supports the idea that the pressure dependence of the host-host exchange interaction is unimportant.[5] This failure of the PCM is not understood, however, in terms of early neutron scattering at atmospheric pressure studies which have shown that the host fourth-order crystalline-field parameter B_4 in the Van Vleck pnictides is inversely proportional to some power n ($n \simeq 5$) of the lattice constant.[4] Also previous Er^{3+} ESR studies in various pnictides[10] have shown that the ratio B_4/B_6 can be understood by the PCM. This, however, should be regarded with caution because ESR measurements are incapable

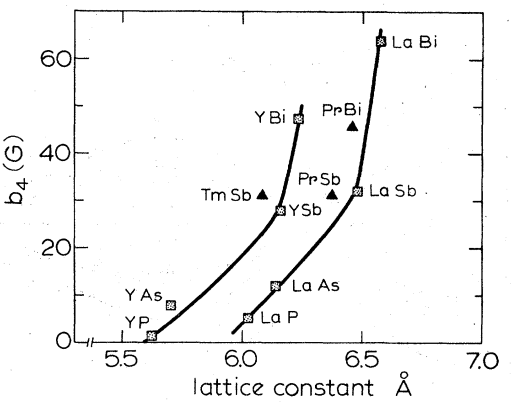

FIG. 4. Plot of the values of b_4 of Gd in various pnictides vs the host lattice constant. The values of b_4 for the nonmagnetic pnictides were taken from Refs. 1 and 2. The solid lines are guide to the eye.

of separating between the fourth order parameter B_4 and the sixth-order parameter B_6.

Using our data in Fig. 4, we have estimated the "average" derivative of b_4 with respect to the lattice constant, $d(\ln b_4)/d(\ln a)$. For LaAs:Gd, we have estimated this value to be approximately 12. In the case of the antimonides (PrSb:Gd, YSb:Gd, and LaSb:Gd) the estimation is difficult because the antimonides are sitting in Fig. 4 on the intersection of two different slopes. For PrSb we have estimated $d(\ln b_4)/d(\ln a)$ to be $\simeq 12$ from the lower slope and $\simeq 60$ from the higher slope. It is not clear to what extend the pressure derivative of b_4 is related to the pressure derivative of B_4 of the host. It is interesting, however, to compare our value with the pressure derivative of the Γ_1-Γ_4 splitting of the host Pr in PrSb as found by Vettier *et al.*[7] These authors have observed a $d[\ln E(\Gamma_1 - \Gamma_4)]/d(\ln a) = 13$ for $\vec{q} = 0$. Thus, if the lattice constant dependence of b_4 reflects that of B_4, then the value of Vettier *et al.* is consistent with the lower slope for PrSb and also with the value of $d(\ln b_4)/d(\ln a)$ found for LaAs.

The Gd fourth-order crystalline-field parameter, b_4, and the Gd Korringa relaxation rates, $\Delta H_K/T$, have been studied systematically recently in the analogue nonmagnetic pnictides LaX:Gd, YX:Gd, and LuX:Gd ($X = P$, As, Sb, Bi) and were found to vary significantly with the host lattice constant.[3] We have summarized the data and have plotted in Fig. 5 the value of b_4 vs $\Delta H_K/T$ as measured in the same host. A remarkable correlation is observed: the value of b_4 was found to increase almost linearly with the increase of $\Delta H_K/T$ (Fig. 5). Unfortunately the Korringa thermal broadening in the Van Vleck pnictides could not be measured because of complete dominance of relaxation processes associated with fluctuations of the

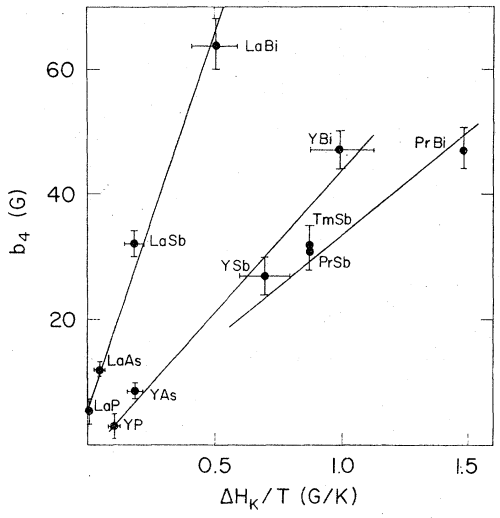

FIG. 5. Plot of b_4 of Gd in the Van Vleck pnictides and in the analogous notmagnetic pnictides versus the Korringa relaxation rates are measured for the same hosts.

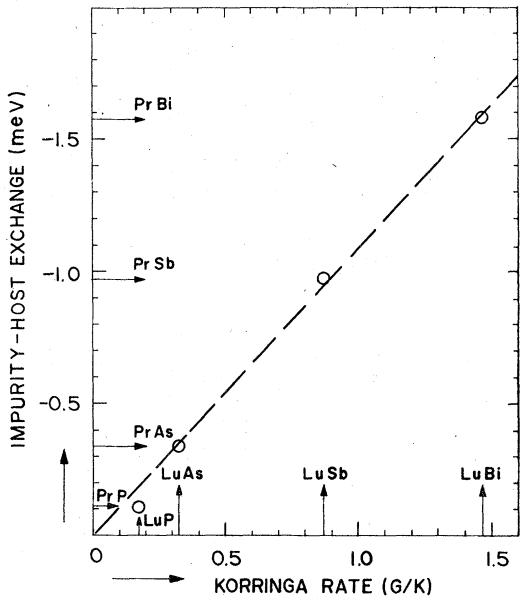

FIG. 6. Correlation between the Gd-Pr exchange interaction, $J_{Gd\text{-}Pr}$, measured in the Van Vleck pnictides and the Gd Korringa thermal broadening, $\Delta H_K/T$, as measured in analogue nonmagnetic LuX (X= P, As, Sb, Bi) pnictides.

host rare-earth ions.[8] In the absence of this information we have plotted in Fig. 5 the values of b_4 for PrSb:Gd (TmSb:Gd) and PrBi:Gd against the Korringa relaxation rates found for LuSb:Gd and LuBi:Gd, respectively.[3] The functional dependence of b_4 vs $\Delta H_K/T$ is consistent with that found in the analogous nonmagnetic pnictides (Fig. 5). The correlation between b_4 and $\Delta H_K/T$ is amazing and the first of its kind in the ESR of any metal. The Korringa relaxation rate depends on the square of the density of states and the local moment-conduction electrons exchange parameter.[3] The latter parameter have been shown to depend on overlap of wave function of d character originating from neighboring sites in the pnictides.[3] Thus the correlation observed strongly supports the idea that b_4 is associated with conduction-electron effects and that the variation of b_4 upon changing the lattice constant a is a consequence of the dramatic change of the d-d overlap or even the local density of states at the impurity site.

We turn now to discuss the exchange interaction, $J_{Gd\text{-}Pr}$. Similar to our plot in Fig. 5, we have plotted in Fig. 6 the values of $J_{Gd\text{-}Pr}$ as extracted from our study (and those of others[9]) versus the Korringa relaxation rate of LuX:Gd (X = P, As, Sb, Bi).[3] Again, a remarkable linear increase of $J_{Gd\text{-}Pr}$ vs $\Delta H_K/T$ is observed. This indicated that $J_{Gd\text{-}Pr}$ is mediated via conduction electrons. Similar to the case of b_4 we believe that the change of $J_{Gd\text{-}Pr}$ upon changing the lattice constant is associated with the strong variation in the d-d overlap.

We have estimated also the value of $d(\ln J_{Gd\text{-}Pr})/d(\ln a)$ using the plot of $J_{Gd\text{-}Pr}$ versus the lattice constant in Refs. 11 and 12. We found for PrAs:Gd that $d(\ln J_{Gd\text{-}Pr})/d(\ln a)$ is equal to 10 ± 3. Thus the pressure derivative of $J_{Gd\text{-}Pr}$ (from ESR data) have the same order of magnitude as the pressure derivative of b_4. This indicate that if our measured values reflects the pressure dependence of B_4 and $J_{RE\text{-}RE}$ then it is not obvious that the pressure dependence of $J_{RE\text{-}RE}$ is not important.[5]

In conclusion, we have demonstrated that both the fourth-order crystalline-field parameter b_4 and the Gd-host exchange interaction can not be described by the point charge model in agreement with previous observations. We suggest that conduction-electron effect are probably responsible for the anomalous variation of b_4 and $J_{Gd\text{-}Pr}$ with lattice constant. We have shown that $d(\ln J_{Gd\text{-}Pr})/d(\ln a)$ and $d(\ln b_4)/d(\ln a)$ have roughly the same order of magnitude and are large enough to justify ESR study under pressure. Such measurement are conducted currently in our laboratory.

ACKNOWLEDGMENTS

This work has been supported by CNPq and FAPESP. One of us (D. D.) has been supported by the U. S.-Israel Binational Science Foundation.

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