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 \( b \) was found to increase with the lattice constant upon going from the antimonides to the bismuthides, consistent with the variation of \( b \) in the analogous nonmagnetic pnictides. A correlation between \( b \) and the Korringa rate in the analogous nonmagnetic compounds suggests that the variation of \( b \) 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 \( b \) 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 \( b \) 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\(^{5,7} \) we were able to demonstrate the existence of a correlation between \( b \) and the Korringa relaxation rate as measured in the same hosts.\(^{5} \) Such a correlation suggests that the variation of \( b \) 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.\(^{5-7} \)

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:

\[
\mathcal{H} = g \mu_B \mathbf{H} \cdot \mathbf{S}_{\text{Gd}} + \sum_{\text{RE}} J_{\text{Gd-RE}} \mathbf{S}_{\text{RE}} \cdot \mathbf{S}_{\text{Gd}} + \left( \frac{1}{60} \right) b (O_{1}^2 + 5O_{1}^4),
\]

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 \( O_{1}^2 \) and \( O_{1}^4 \) as spin operators of the fourth degree. We have assumed in our analysis...
that $J_{04,\text{RE}}$ 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

$$H(\pm \frac{1}{2} \Rightarrow \pm \frac{1}{2}) = H' \pm 20(1 - 5\phi)b_4,$$

$$H(\pm \frac{1}{2} \Rightarrow \pm \frac{3}{2}) = H' \pm 10(1 - 5\phi)b_4,$$

$$H(\pm \frac{3}{2} \Rightarrow \pm \frac{1}{2}) = H' \pm 12(1 - 5\phi)b_4,$$

$$H(\pm \frac{1}{2} \Rightarrow \mp \frac{1}{2}) = H',$$

where

$$H' = H_0\left[1 + \frac{1}{2} + \frac{1}{2} / (gJ - 1)/gJ \chi_{VV}/\mu_B^2N_0\right]_{\text{Gd-RE}}.$$

Here $H_0$ is the external field, $g_J$ is the Landé $g$ factor of the host rare-earth ions, $\mu_B$ is the Bohr magneton, and $\chi_{VV}$ is the host Van Vleck susceptibility. $I$, $m$, 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 $\frac{1}{2} \rightarrow -\frac{1}{2}$, $\frac{1}{2} \rightarrow -\frac{3}{2}$, $\frac{3}{2} \rightarrow -\frac{1}{2}$, $\frac{3}{2} \rightarrow -\frac{3}{2}$ 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 $b_4(\text{PrBi:Gd}) = 47 \pm 4$ G, $b_4(\text{PrSb:Gd})$.

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 $\frac{1}{2} \rightarrow -\frac{3}{2}$ and $\frac{3}{2} \rightarrow -\frac{1}{2}$ always appear as overlapping lines in our spectra. The measurements were performed at frequency of 9.063 GHz.

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 $\frac{1}{2} \rightarrow -\frac{3}{2}$ and $\frac{3}{2} \rightarrow -\frac{1}{2}$ 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.
$= 31 \pm 3 \text{ G}$, and $b_4^{(\text{TmSb:Gd})} = 32 \pm 2 \text{ G}$.

The value of $b_4$ for PrSb:Gd is consistent with that found previously.\textsuperscript{8} The error bar, however, is much smaller because of the much better resolution of our ESR spectra. The values of $d_{\alpha=\Bb}$ are consistent with those reported by Rettori et al. and Sugawara et al.\textsuperscript{3} 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 nonmagnetic pnictides measured previously.\textsuperscript{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 splitting configuration state into the ground $S$ state via the spin-orbit coupling.\textsuperscript{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.\textsuperscript{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\textsuperscript{3} and a very recent neutron scattering under pressure by Vettier et al.\textsuperscript{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.\textsuperscript{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 $n$ ($n \approx 5$) of the lattice constant.\textsuperscript{4} Also previous $\text{Er}^{3+}$ ESR studies in various pnictides\textsuperscript{8} have shown that the ratio $B_4/B_2$ can be understood by the PCM. This, however, should be regarded with caution because ESR measurements are incapable 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 $\approx 12$ from the lower slope and $\approx 60$ 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 $\Gamma_5-\Gamma_1$ splitting of the host Pr in PrSb as found by Vettier et al.\textsuperscript{1} These authors have observed a $d(\ln E(\Gamma_5 - \Gamma_1))/d(\ln a) = 13$ for $\Gamma = 0$. Thus, if the lattice constant dependence of $b_4$ reflects that of $B_4$, then the value of Vettier et al.\textsuperscript{1} 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, $\Delta H_E/T$, 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.\textsuperscript{3} We have summarized the data and have plotted in Fig. 5 the value of $b_4$ vs $\Delta H_E/T$ 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 $\Delta H_E/T$ (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
host rare-earth ions. 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. The functional dependence of $b_4$ vs $\Delta H_p/T$ is consistent with that found in the analogous nonmagnetic pnictides (Fig. 5). The correlation between $b_4$ and $\Delta H_p/T$ 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. The latter parameter have been shown to depend on overlap of wave function of d character originating from neighboring sites in the pnictides. 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, $J_{Gd-Pr}$. Similar to our plot in Fig. 5, we have plotted in Fig. 6 the values of $J_{Gd-Pr}$, as extracted from our study (and those of others) versus the Korringa relaxation rate of LuX:Gd ($X = P, As, Sb, Bi$). Again, a remarkable linear increase of $J_{Gd-Pr}$ vs $\Delta H_p/T$ is observed. This indicated that $J_{Gd-Pr}$ is mediated via conduction electrons. Similar to the case of $b_4$ we believe that the change of $J_{Gd-Pr}$ upon changing the lattice constant is associated with the strong variation in the d-d overlap.

We have estimated also the value of $d(\ln J_{Gd-Pr})/d(\ln a)$ using the plot of $J_{Gd-Pr}$ versus the lattice constant in Refs. 11 and 12. We found for PrAs:Gd that $d(\ln J_{Gd-Pr})/d(\ln a)$ is equal to 10 + 3. Thus the pressure derivative of $J_{Gd-Pr}$ (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 $J_{RE-RE}$ then it is not obvious that the pressure dependence of $J_{RE-RE}$ is not important.

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 $J_{Gd-Pr}$ with lattice constant. We have shown that $d(\ln J_{Gd-Pr})/d(\ln a)$ 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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