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Dynamical interactions in $EuAsO_4(Gd)$ and $EuVO_4(Gd)$

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Electron-paramagnetic-resonance experiments on Gd^{3+} impurities in the singlet-ground-state zircon systems $EuAsO_4$ and $EuVO_4$ have been used to study the various possible dynamical interactions in these systems. The low-lying degenerate excited states of Eu^{3+} in these compounds can produce dynamical electric, magnetic, and exchange fields in the lattice. From the ratios of the linewidths in the fine-structure spectra of $EuAsO_4(Gd)$ and $EuVO_4(Gd)$, we find that the dynamical magnetic and/or exchange fields are dominant over the dynamical electric fields caused by the Jahn-Teller effect. From the relative magnitudes of the linewidths in the two compounds, we conclude that exchange interactions are more important than the magnetic dipolar effects.

I. INTRODUCTION

Electron paramagnetic resonance has primarily been used in the past to study paramagnetic impurities in diamagnetic hosts. Ths use of paramagnetic crystals has been largely avoided out of the concern for unmanageably wide resonance lines caused by the interactions between the impurities and the paramagnetic host ions. However, in many cases, this concern may not be justified since various mechanisms exist which tend to reduce the strength of the impurity-host interactions. Recently, EPR has been used to study *S*-state ion impurities in crystals which manifest the cooperative Jahn-Teller effect, both below[1] and above[2,3] phase transitions. Below phase transitions, uniform strains split the degenerate ground states, rendering them nonmagnetic in the absence of an external field. Above phase transitions, interactions of the Jahn-Teller ions with phonons produce dynamic nonuniform strains.[2,3] Thus, at a given time and site the levels are split and nonmagnetic, although the applied magnetic field induces a magnetic moment which is field dependent.[3] In general this kind of splitting is dynamic, since there are always mechanisms which transform one set of distortions to a different set. The transformations will have a spectrum of associated frequencies, and only for the low-frequency components the distortions can be regarded as static.

In compounds with degenerate ground-state ions, where the magnetic or exchange interactions between the ions are larger than the phonon-induced Jahn-Teller interactions, a magnetic rather than a Jahn-Teller phase transition takes place. The two types of interactions, magnetic and Jahn-Teller, are to a large extent mutually exclusive

A slightly different situation arises when the ground state of the host ion is nondegenerate but excited degenerate states are nearby.[4,5] In this case, at temperatures where the degenerate states are populated, the broadening of the impurity lines may again arise from either the Jahn-Teller induced random strains or the dipolar and exchange effects, and these effects are almost always dynamic.

In a recent paper[6] on the temperature dependence of the EPR spectrum of the singlet-triplet samarium chalcogenide systems $SmS(Eu^{2+})$ and $SmSe(Eu^{2+})$, we mentioned the above possible sources of line broadening at high temperatures. It is difficult, however, in those systems, to determine which of the suggested mechanisms is the dominant one. This difficulty arises from the fact that the fine-structure spectrum of Eu^{2+} is complicated by two overlapping hyperfine spectra due to the interactions with the 48% abundant ^{151}Eu and 52% abundant ^{153}Eu nuclei with nuclear spins $\frac{5}{2}$. Furthermore, the Eu^{2+}-Sm^{2+} exchange interactions which contribute to the linewidths are too large.

These problems are alleviated if one works instead with the tetragonal zircon systems $EuAsO_4(Gd^{3+})$ and $EuVO_4(Gd^{3+})$, where the Eu^{3+} ions have the same electronic configuration $(4f^6\,{}^7F)$ as the Sm^{2+} ions in the chalcogenides and the Gd^{3+} impurities $(4f^7\,{}^8S)$ are equivalent to the Eu^{2+} impurities. The hyperfine interactions with the 15% abundant ^{155}Gd and 16% abundant ^{157}Gd with nuclear spins $\frac{3}{2}$ are much smaller than those in Eu, and the impurity-host exchange interactions are much smaller than those in the chalcogenides. An added advantage of the zircon structure, D_{4h}^{19}, is that its lower symmetry (tetragonal) compared to that of the chalcogenides (cubic) simplifies the analysis of the spectra. At the same time, a minimum (doublet) degeneracy is left in a nearby excited level of Eu^{3+} to retain the interesting effects arising from degeneracies. The third member of this group $EuPO_4$ has a monoclinic struc-

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ture and the degeneracies in Eu^{3+} levels are, therefore, completely removed.

In this paper we report on the EPR studies in $EuAsO_4(Gd)$ and $EuVO_4(Gd)$. We analyze the possible relationships between the widths of the various lines of the fine-structure spectra in each compound in terms of the dynamical Jahn-Teller induced random strain effects and the fluctuating dipolar or exchange interactions. We find that the experimental results agree with the latter mechanisms. A comparison between the *magnitudes* of the linewidths of the two compounds favors dynamical exchange to dynamical dipolar effects as the main source of the lifetime line broadenings.

II. EXPERIMENTAL RESULTS

EPR experiments were performed on $\sim 1\times 1\times 3$ mm^3 flux grown, Gd-doped $EuAsO_4$ and $EuVO_4$ single crystals with ~1000-ppm Gd/Eu at ~9 GHz and $6 < T < 550$ K. Crystal-field effects split the eightfold degenerate state of Gd^{3+} into four Kramers doublets. In the presence of a strong external magnetic field there are seven $\Delta M_S = \pm 1$ allowed transitions among the eight separated energy levels. These are shown at low temperatures in Figs. 1(a) and 1(b) for $EuAsO_4(Gd)$ and $EuVO_4(Gd)$ with magnetic fields applied along the c axes.

The spectrum of Gd^{3+} substituting for Eu^{3+} with a D_{2d} point symmetry can be analyzed by the tetragonal spin Hamiltonian

$$\mathcal{H}_{\mathrm{Gd}} = \mu_B[g_\perp(H_xS_x + H_yS_y) + g_\parallel H_zS_z] + B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4 \; . \qquad (1)$$

The measured g values are shown in Fig. 2. No anisotropies in g values were observed within the experimental errors (i.e., $g_\parallel = g_\perp = g$). At low temperatures there are g shifts from the normal Gd^{3+} g value of ~1.992 in diamagnetic hosts. These shifts are caused by the induced magnetic moment in the Eu^{3+} Γ_1 singlet ground state ($J = 0$), because the field generated by the Gd^{3+} magnetic moment admixes the

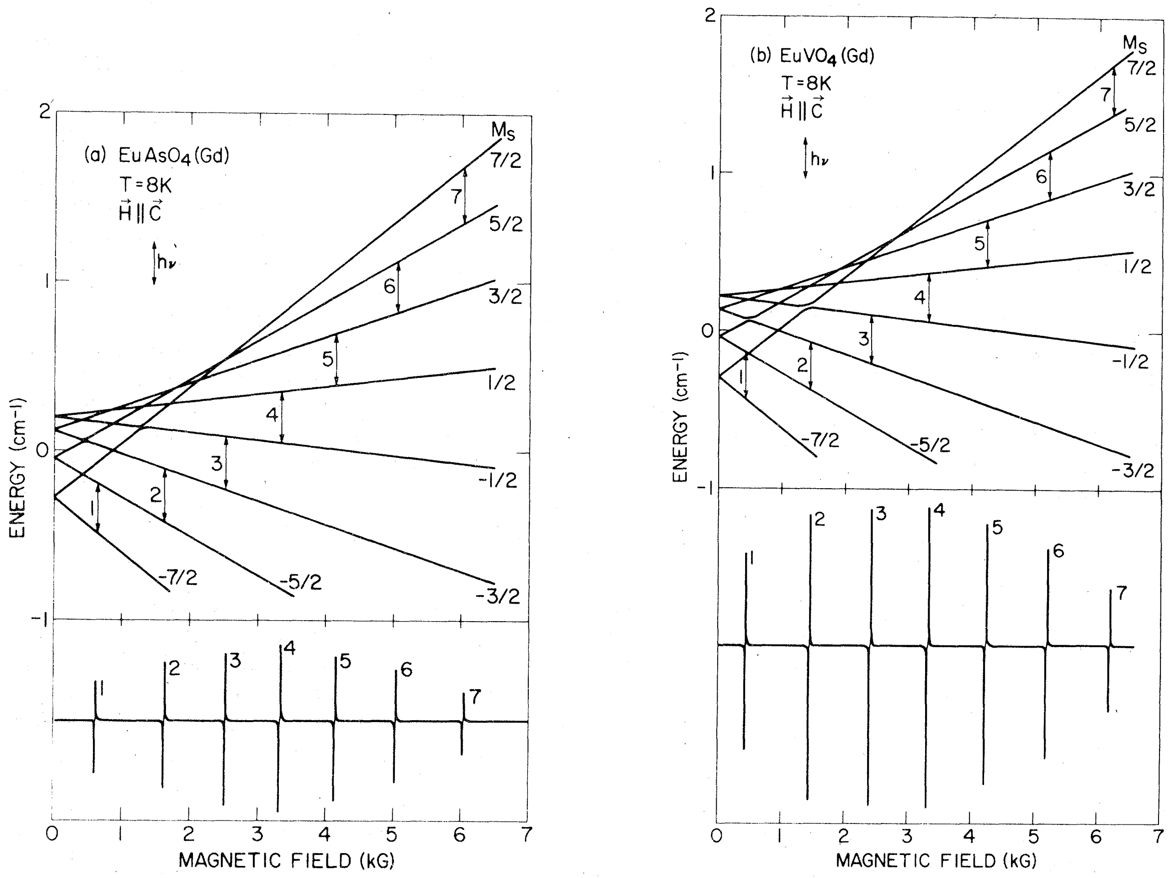

FIG. 1. Energy levels and observed fine-structure spectra with the magnetic field parallel to the c axis at 8 K in (a) $EuAsO_4(Gd)$ and (b) $EuVO_4(Gd)$.

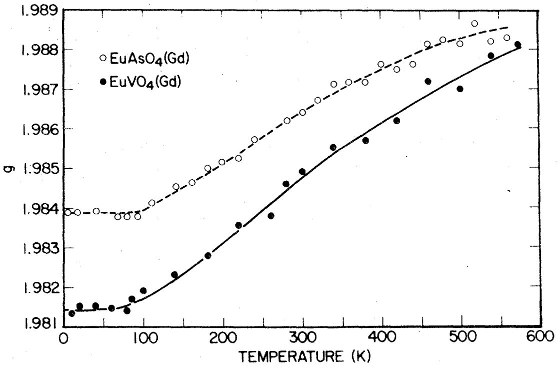

FIG. 2. Temperature dependence of g values in EuAsO$_4$(Gd) and EuVO$_4$(Gd).

crystal-field-split $J=1$ state of Eu^{3+} ions into its ground state.[7] For the external magnetic field parallel to the c axis, the shifts are due to the admixtures of the excited Γ_2 singlets into the ground Γ_1 states. The first excited (Γ_2) states are at ~353 cm^{-1} for EuAsO$_4$,[8] and ~334 cm^{-1} for EuVO$_4$.[9] The observed g shifts are much smaller than, and of opposite sign (antiferromagnetic) to, those observed for the rare-earth impurities in samarium chalcogenides.[10,11] These differences confirm the importance of the 5d conduction band as an intermediary for the Sm^{2+}-Eu^{2+} exchange in the samarium chalcogenides.[12] In EuAsO$_4$ and EuVO$_4$, which are good insulators, the 5d bands are far away and ineffective. The temperature variations of the g shifts (Fig. 2), for external fields parallel to the c axes, can be explained in terms of a theory developed in Ref. 6 based on an inverse magnetic moment induced in the first excited singlet state due to the admixture of the singlet ground state into the excited state by the Gd^{3+} impurity. The temperature dependence of the H shifts are shown in Fig. 3 and agree with the theoretical expression[6]

$$\delta H(T)=\delta H(0)(1-e^{-\Delta/kT})/(1+e^{-\Delta/kT}) , \qquad (2)$$

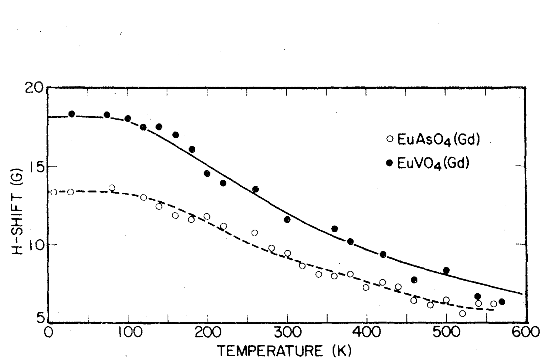

FIG. 3. Experimental (points) and theoretical (lines) H shifts in EuAsO$_4$(Gd) and EuVO$_4$(Gd).

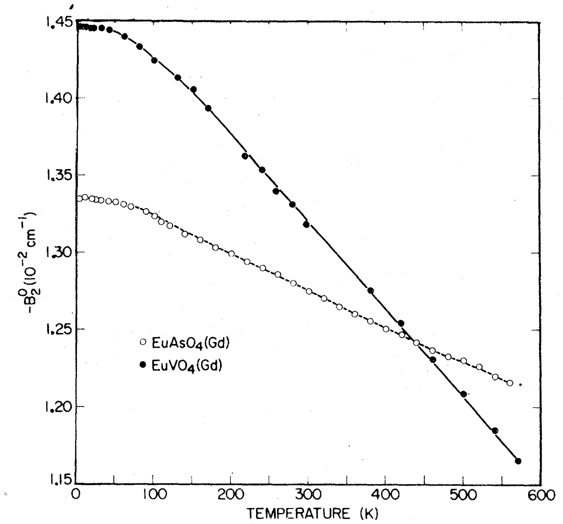

FIG. 4. Temperature dependence of the axial crystal-field parameter B_2^0 in EuAsO$_4$(Gd) and EuVO$_4$(Gd).

where Δ is the energy difference between the first excited and the ground singlets of Eu^{3+} and $\delta H(0)$ is the experimentally determined shifts of the centers of the resonances at low temperatures from their normal value (i.e., H corresponding to $g=1.992$).

The temperature dependences of the axial crystal-field parameters B_2^0 are shown in Fig. 4 and the other crystal-field parameters are given in Table I. The general characteristics of the temperature variations of the crystal-field parameters are quite normal and are probably due to phonon effects.[13]

The temperature dependences of the linewidths in the fine-structure spectra of EuAsO$_4$(Gd) and EuVO$_4$(Gd) are shown in Fig. 5. The line shapes at high temperatures are accurately Lorentzian. They deviate slightly from Lorentzian as the temperature is lowered. At the lowest temperatures all seven lines in the fine structure are of the same width and are 8.2 ± 0.2 G for EuAsO$_4$(Gd) and 9.7 ± 0.7 G for EuVO$_4$(Gd). These residual linewidths at low temperatures are caused by hyperfine interactions with ^{155}Gd and ^{157}Gd, superhyperfine interactions with ^{75}As or ^{51}V, and finally the remnant Gd^{3+}-Gd^{3+} dipolar interaction, although the contribution from the latter is expected to be very small in our highly diluted samples.

At high temperatures the widths of the seven lines in each fine structure are different. From their ratios (once the low-temperature linewidths are subtracted) and from the magnitudes of the linewidths, one can determine which one of the possible sources of line broadening is dominant. This will be discussed in Sec. III.

TABLE I. Measured crystal-field parameters for Gd^{3+} (cm^{-1}).

	$EuAsO_4$	$EuVO_4$
B_4^0	$(-7.2 \pm 0.1) \times 10^{-6} + (1.4 \pm 0.3) \times 10^{-9} T$ (K)	$(-3.7 \pm 0.1) \times 10^{-6} + (1.1 \pm 0.3) \times 10^{-9} T$ (K)
B_4^4	$(1.13 \pm 0.1) \times 10^{-4} - (3.2 \pm 0.2) \times 10^{-8} T$ (K)	$(1.12 \pm 0.1) \times 10^{-4} - (7.0 \pm 0.2) \times 10^{-8} T$ (K)
B_6^0	$(3.4 \pm 0.2) \times 10^{-8}$	$(3.8 \pm 0.5) \times 10^{-8}$
B_6^4	$(-2.0 \pm 0.4) \times 10^{-7}$	$(-6 \pm 3) \times 10^{-8}$

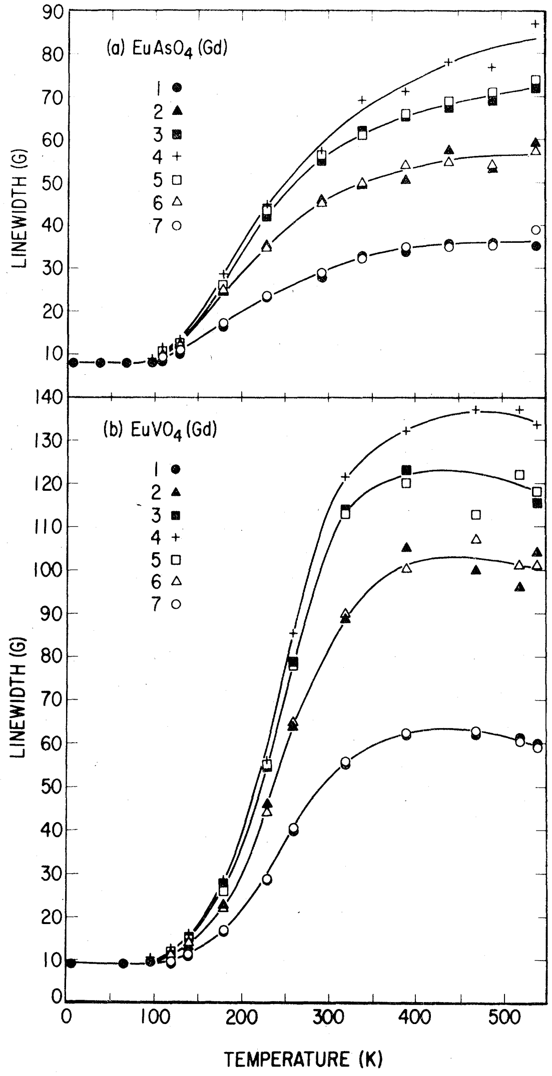

FIG. 5. Temperature dependence of linewidths for the fine-structure spectra in (a) $EuAsO_4$(Gd) and (b) $EuVO_4$(Gd). The numbers in 1 to 7 refer to the transitions shown in Fig. 1.

III. THEORY

Since the g shifts are temperature dependent, it is expected that the linewidths should also have a temperature dependence due to this source.[6] A second moment analysis gives this linewidth as

$$\Delta H|_{g\ \text{shift}} = \frac{\delta H(0)}{\sqrt{3}} \frac{e^{-\Delta/2kT}}{1+e^{-\Delta/kT}} . \tag{3}$$

Although this may be an important source of line broadening for impurities in samarium chalcogenides with large g shifts,[10,11] it is much less important for $EuAsO_4$(Gd) and $EuVO_4$(Gd), which have very small g shifts. The linewidth at high temperatures from Eq. (3) is only about 3 to 4 G. Furthermore, the analysis leading to Eq. (3) ignores thermal relaxations between the excited and the ground states, which tend to modulate and reduce this linewidth to even lower values.[6] This kind of broadening is, therefore, completely negligible for the present case. Spin-lattice relaxations on Gd^{3+} ions can also be ignored since no temperature variation is observed in the linewidths of the *diamagnetic* systems $YAsO_4$(Gd) and YVO_4(Gd) in the temperature range $6 < T < 550$ K.

There remain the fluctuating B_2^2 strain fields from the Jahn-Teller interactions[2-4] and the fluctuating B_1^1 dipolar or exchange fields, all generated by the Eu^{3+} ions when their first excited Γ_5 doublets become populated. These doublets are at ~380 cm^{-1} for $EuAsO_4$,[8] and ~376 cm^{-1} for $EuVO_4$.[9] As already mentioned, these two classes of mechanisms for line broadening are to a large degree mutually exclusive for if the Jahn-Teller effect is stronger, the Γ_5 levels at a given time are split and the dipolar and exchange effects are reduced, whereas if the latter effects are stronger the levels are split by them and then the Jahn-Teller effect is diminished. It is therefore reasonable to consider the two classes separately and compare the results with the experiment to determine the dominant mechanism.

The fluctuating B_2^2 field from the Jahn-Teller effect produces $\Delta M_S = \pm 2$ transitions in the energy levels of

Gd^{3+} shown in Fig. 1. The dipolar and/or exchange fields produce a fluctuating B_1^1 field which cause $\Delta M_S = \pm 1$ transitions in the energy levels. These effects cause lifetime broadenings in the energy levels which in turn contribute to the linewidths of the spectrum. This corresponds to the *nonsecular* broadening described by Kubo and Tomita.[14] The *secular* broadening is negligible since the low-frequency components of the fluctuating fields parallel to the applied field have small amplitudes.

To determine the total lifetimes for each energy level, it is necessary to calculate the partial lifetimes for every possible transition to other levels. A Green function analysis,[15] shows that the inverse resultant lifetime for each level is the sum of the inverses of these partial lifetimes, and the resultant linewidth for each transition between two energy levels is the sum of the lifetime broadenings of the two energy levels. Further, this analysis predicts the line shapes to be Lorentzian.

For a Gd^{3+} energy level with the magnetic quantum number M_S, the lifetime broadening from a dynamic B_1^1 field is due to the transitions to $M_S \pm 1$ levels. The transition probabilities are proportional to

$$|\langle M_S \pm 1 | S_\pm | M_S \rangle|^2 .$$

The lifetime broadening of the M_S level is therefore

$$\Delta H(M_S) = \Delta H_+ + \Delta H_- = a(|\langle M_S + 1 | S_+ | M_S\rangle|^2 + |\langle M_S - 1 | S_- | M_S \rangle|^2). \quad (4)$$

The width of the line corresponding to the transition $M_S \leftrightarrow M_S - 1$ is

$$\Delta H(M_S \leftrightarrow M_S - 1) = \Delta H(M_S) + \Delta H(M_S - 1) = b[2S(S+1) - 2M_S(M_S - 1) - 1] . \quad (5)$$

For a fluctuating B_1^2 field the lifetime broadenings are due to transitions $\Delta M_S = \pm 2$. The transition probabilities are proportional to: $|\langle M_S \pm 2 | S_\pm^2 | M_S \rangle|^2$.

TABLE II. Theoretical linewidths from fluctuating dipolar or exchange effects (ΔH) and dynamical Jahn-Teller effects ($\Delta' H$) calculated from Eqs. (5) and (7).

Transition	$\Delta H/b$	$\Delta' H/d$
$\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$	13	66
$\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$	23	126
$\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$	29	186
$\frac{1}{2} \leftrightarrow -\frac{1}{2}$	31	210

The lifetime broadening of the M_S level is

$$\Delta'(M_S) = \Delta' H_+ + \Delta' H_- = c(|\langle M_S + 2 | S_+^2 | M_S \rangle|^2 + |\langle M_S - 2 | S_-^2 | M_S \rangle|^2) . \quad (6)$$

The width of the line corresponding to the transition $M_S \leftrightarrow M_S - 1$ is

$$\Delta' H(M_S \leftrightarrow M_S - 1) = \Delta' H(M_S) + \Delta' H(M_S - 1) = d[x^2y^2 + 2 + (y+1) \times (2x^2 - 5x + y + 1)] , \quad (7)$$

where $x = S + M_S$ and $y = S - M_S$.

Table II shows the theoretical linewidths predicted by Eqs. (5) and (7). By taking the ratios of the theoretical linewidths the constants b and d are eliminated and the theoretical ratios can be compared with the experimental ratios, once the low-temperature widths are subtracted from the experimental values. These are given in Table III, which shows excellent agreement between the experimental results and the predictions of a fluctuating B_1^1 field. It is not possible, however, to distinguish between

TABLE III. Theoretical and experimental linewidth ratios.

	Theory		Experiment	
	Dipolar or exchange	Jahn-Teller	EuAsO$_4$(Gd)	EuVO$_4$(Gd)
$+\frac{1}{2} \leftrightarrow -\frac{1}{2} / \pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$	2.38	3.18	2.40 ± 0.08	2.39 ± 0.07
$\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2} / \pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$	2.23	2.82	2.20 ± 0.06	2.23 ± 0.03
$\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2} / \pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$	1.77	1.91	1.73 ± 0.06	1.76 ± 0.05

exchange and dipolar effects by this method since they both produce a fluctuating B_1^1 field at the Gd positions. On the other hand, since the lattice constants for $EuAsO_4$ and $EuVO_4$ are comparable, one expects the dipolar effects to produce comparable fields. The experimental results (Fig. 5), however, show that the widths are much larger for $EuVO_4$(Gd) than for $EuAsO_4$(Gd). The Gd^{3+}-Eu^{3+} exchange interaction in the two compounds can be quite different. It is known, for example, that the Gd-Gd exchange interaction in $GdVO_4$[16] is about a factor of 2 larger than the exchange in $GdAsO_4$.[17] Since the high-temperature linewidths in $EuVO_4$(Gd) are about twice as large as the linewidths in $EuAsO_4$(Gd) (Fig. 5), it appears that the dominant mechanism for Gd^{3+} line broadening in these compounds is the fluctuating exchange interaction.

IV. CONCLUSIONS

We have shown that the temperature variations of the linewdiths of the fine structure of *S*-state ion impurities in zircon systems containing Van Vleck ions with low-lying degenerate excited states may be used to determine the predominant dynamical interactions in these systems. In general, the fluctuating fields at the impurity positions may be divided into two groups: (a) those arising from the Jahn-Teller induced dynamical random strains which induce $\Delta M_S = \pm 2$ transitions in the impurity energy levels; (b) those arising from the fluctuating magnetic dipolar and/or exchange fields producing a $\Delta M_S = \pm 1$ transition in the impurity energy levels. Other sources of line broadening are either negligible or can be subtracted. These two types of mechanism for lifetime (nonsecular) line broadening produce different ratios of linewidths in the various lines of the fine-structure spectra. In the systems $EuAsO_4(Gd^{3+})$ and $EuVO_4(Gd^{3+})$, we have shown that the difference between the high-temperature and low-temperature linewidths can be attributed to the fluctuating perpendicular magnetic fields at Gd^{3+} and that the secular (longitudinal) effects are negligible. It is not possible, on purely linewidth ratio arguments, to distinguish between dipolar and exchange effects since they both produce fluctuating B_1^1 fields at the impurity sites. However, from the magnitudes of the linewidths which are larger in $EuVO_4$(Gd) than in $EuAsO_4$(Gd) it appears that exchange rather than dipolar effects are dominant since the latter are expected to be comparable in the two compounds.

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