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Random Strain Effects in the Cooperative Jahn-Teller System $TmVO_4$

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Electron-paramagnetic-resonance studies of the cooperative Jahn-Teller system $TmVO_4$ doped with Gd indicate that in the high-temperature phase the behavior of the spectrum is probably dominated by the presence of random strains arising from the Jahn-Teller effect. The random strain effects in these systems have so far been largely neglected.

Cooperative Jahn-Teller effects in compounds with tetragonal zircon structure containing rare-earth ions have recently been of great interest[1] both because of their novelty and their amenability to simple theoretical considerations. Most of the analyses, however, have been concentrated on the behavior near or below the phase transition where the effect of the *uniform* strains are most important. The interesting effects due to the presence of *random* strains in the high-temperature phase have been rather neglected. In this Letter we report on the electron-paramagnetic-resonance studies of $TmVO_4(Gd^{3+})$ in the high-temperature tetragonal phase and propose that the anomalous temperature variations of linewidths are probably due to the existence of random strains arising from the Jahn-Teller effect.

$TmVO_4$ is the closest material to an ideal cooperative Jahn-Teller system. The ground state of the Tm^{3+} ion is an electronic doublet well separated, $\sim 54\ cm^{-1}$, from the first (singlet) excited state. Because of small electron-phonon interaction with nondegenerate lattice modes of symmetry B_{2g} the compound undergoes a tetragonal to orthorhombic transition at $T_c = 2.1$°K. For EPR studies the compound has been doped with Gd^{3+} which has an $^8S_{7/2}$ configuration and can be observed in a wide temperature range and also has charge and size compatibility with Tm^{3+} which it replaces. The spectra of $TmVO_4(Gd)$ have previously been reported at 1.5°K in the low-symmetry phase by Schwab.[2] At that temperature the thermally occupied level of Tm^{3+} is, in zero magnetic field, a nonmagnetic singlet; hence there should be little dipolar broadening. Furthermore, as we will show, the spectrum below T_c is not broadened by random strains and the observation thus seems to present no problems.

Our experiments were performed at 9 GHz in a temperature range of $2°K < T < 570$ °K. However, below ~110°K the spectra were washed out due to excessive line broadening. The crystals were grown by the flux method and contained ~1000

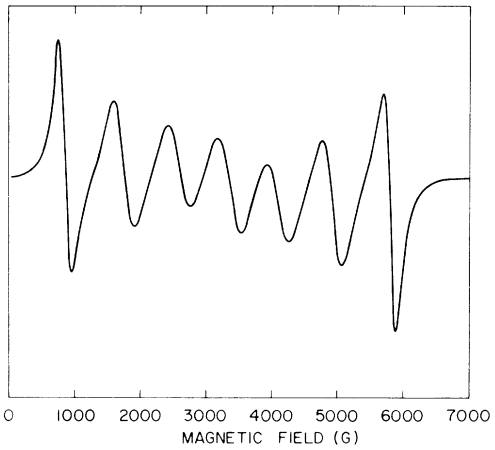

FIG. 1. The fine structure of $TmVO_4(Gd^{3+})$ at room temperature with the magnetic field along the c axis.

ppm Gd. Figure 1 shows the observed fine structure at room temperature with the magnetic field parallel to the c axis. The spectra showed tetragonal symmetry and were fitted to the tetragonal spin Hamiltonian[3]:

$$\mathcal{H}_{Gd} = \mu_B g \vec{H}\cdot\vec{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4 . \quad (1)$$

The second-order parameter B_2^0 was found to be strongly temperature-dependent and, for the temperature range shown in Fig. 2, followed the approximate linear relationship:

$$B_2^0 = [(-1.49 \pm 0.01)\times 10^{-2} + (7.7 \pm 0.2)\times 10^{-6} T(^\circ\mathrm{K})]\ \mathrm{cm}^{-1} .$$

The other parameters in Eq. (1) were found to be temperature-independent within the experimental errors:

$$g = 1.992 \pm 0.002 ,$$
$$B_4^0 = (-5.2 \pm 0.2)\times 10^{-6}\ \mathrm{cm}^{-1} ,$$
$$B_6^0 = (6 \pm 2)\times 10^{-8}\ \mathrm{cm}^{-1} ,$$
$$B_4^4 = (3.6 \pm 0.4)\times 10^{-5}\ \mathrm{cm}^{-1} ,$$
$$B_6^4 = (-6 \pm 2)\times 10^{-6}\ \mathrm{cm}^{-1} .$$

It should be noted that the observed g value is identical with that of Gd^{3+} in the comparable *diamagnetic* host YVO_4.[4] There is thus no observable g shift due to the exchange interaction with the paramagnetic Tm^{3+} neighbors. On the other hand, the large temperature dependence of B_2^0 is unlikely to be completely due to the temperature dependence of the lattice constant. It is possible that the exchange is temperature-dependent and also affects various fine-structure lines differently resulting in an apparent temperature variation of B_2^0.

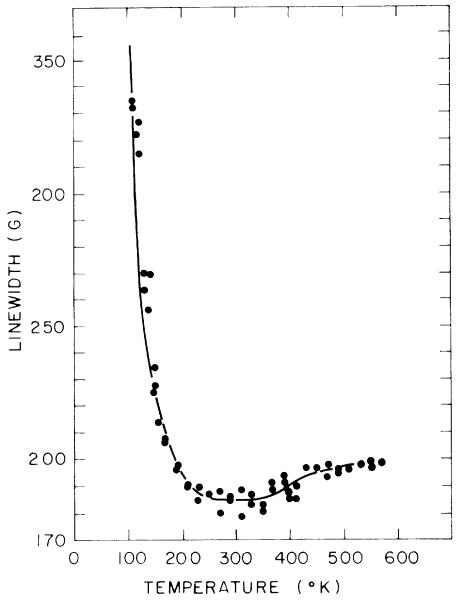

FIG. 2. Temperature dependence of the linewidth for the outer lines of the spectrum shown in Fig. 1.

The most interesting experimental observation is the temperature variation of linewidths. This variation for the outer two lines of the fine structure of Fig. 1 is shown in Fig. 2. The other five lines which are wider show similar behavior, as do the lines for the field in other directions. We will now show that this peculiar temperature dependence may be understood in terms of random strain effects above the phase transition. To see this, it is convenient to assume that each Tm^{3+} ion, located at site n has a single doublet describable by the pseudospin variable[1] $S_z^{(n)}$. Then an effective Hamiltonian is

$$\mathcal{H}_{Tm} = K[(a-L)^2 + (b-L)^2] + \epsilon(a-b)\sum_n S_z^{(n)} + \sum_k \hbar\omega_k \alpha_k^+ \alpha_k + \sum_{k,n} \epsilon_{kn}(\alpha_k + \alpha_{-k}^+) S_z^{(n)} . \quad (2)$$

The first term in Eq. (2), the elastic energy, expresses the requirement that in the absence of coupling of the doublets to the ions the lattice would have a tetragonal unit cell of side L. Thus $a-b$ measures the departure from having tetragonal unit cells. The second term describes the coupling of the

uniform strain to the doublets; and the third and fourth terms, respectively, describe the phonons and interactions of phonons with Tm^{3+} doublets. The phonons are defined as oscillations about the lattice structure in which all unit cells are identical, with sides a and b. Note that all pseudospin operators appearing in $\mathcal{H}_{Tm}$ commute, so that specifying the value of $S_z^{(n)}$ at each point results in an effective Hamiltonian containing only lattice variables. In principle, by a displaced-oscillator transformation,[1] such an expression can be reduced to the form

$$\mathcal{H}_{eff} \equiv \sum_k \hbar\omega_k \beta_k^{+}\beta_k - C_1 - C_2, \quad (3)$$

where C_1 is a Jahn-Teller reduction energy associated with a nonzero value for $a-b$, and C_2 is a Jahn-Teller reduction energy associated with the couplings to the phonons, which now oscillate about displaced lattice sites. It is important to realize that the lattice displacement is composed of two parts. First, there is that due to the uniform strain $a-b$, which is the same for each lattice site. Then there is a second part, which varies from site to site in the lattice, and arises from the pseudospin-phonon coupling. For a different pseudospin arrangement C_1 and C_2 will change; so also will $a-b$ and the local distortion. The vibrations, described by (β^+, β), have the same frequency spectrum as for the uncoupled lattice, but they are vibrations about the distorted lattice.[1] In our experiments, the temperature is above the Jahn-Teller cooperative phase transition point, in which case $\sum_n S_z^{(n)}$ and therefore C_1 are zero. However, since ϵ_{kn} contains[1] $\exp \times (ik\cdot R_n)$, the term $\sum_n \exp(ik\cdot R_n) S_z^{(n)}$ does not usually vanish. There is then no coupling trying to cause a uniform strain, but there are couplings trying (and succeeding) to cause a nonuniform strain.

The Gd^{3+} ions, which presumably substitute for the Tm^{3+} ions in random lattice sites, will experience the nonuniform local strains, and will have rhombic zero-field splitting terms in their spin Hamiltonians. It seems probable that the resultant spectrum will be broadened. However, the above Hamiltonian $\mathcal{H}_{Tm}$ is incomplete, for there must be terms due to other phonon modes which induce pseudospin flips. These will lead to fluctuations in the zero-field splittings of Gd^{3+} ions and, if they occur sufficiently rapidly, the random strain broadening in the Gd^{3+} ions will not be observed. At low temperatures, however, it seems probable that the rate is comparatively slow, so that the random strain broadening is not washed out. In this connection, the energy required to flip a pseudospin is probably quite small, so there are not many phonons "on speaking terms." Also, when a pseudospin is flipped the lattice strain changes slightly, so in any theory there will be overlap integrals between displaced oscillators causing the pseudospin-flip rates to be reduced by Ham[5] reduction factors. Finally, in the experiments of Melcher, Pytte, and Scott[6] ultrasonic waves were used to split the doublets. In their theory it was necessary to allow the populations of the split doublets to return to their equilibrium values with a relaxation time $\tau \sim 10^{-9}$ sec. It thus seems safe to assume that at low temperatures, but above the Jahn-Teller cooperative transition, the random strain broadenings are not washed out. It is necessary to distinguish temperatures above and below cooperative transitions, for below T_c, $\sum_n S_z^{(n)}$ is no longer zero and the $\sum_n \exp(ik\cdot R_n) S_z^{(n)}$ all tend to zero. There is then increasing uniform distortion through the lattice and decreasing random-type strain. The Gd^{3+} zero-field splitting should therefore show a uniform rhombic-type distortion[2] with the random elements associated with the differing sites tending to zero. The random strain broadenings should therefore tend to zero independently of the rate of pseudospin-flip.

In a more realistic picture, each Tm^{3+} ion has more than a single doublet level and it is particularly interesting to ask what happens as the temperature is raised so that another doublet also becomes populated. It is known from the work of Melcher, Pytte, and Scott[6] that the higher-lying doublet at $\sim 198^{\circ}$K is much more strongly coupled to the lattice than the ground doublet. As this excited doublet becomes populated C_2 will become larger, but more importantly the random strain field will become larger in magnitude and probably it will vary much more rapidly with temperature. Apart from the usual increase in relaxation rate, associated with increased phonon occupation numbers, there is now a possibility of transitions between the two doublets, induced by strongly coupled phonons which are beginning to be thermally excited. The EPR results strongly suggest a washing-out of random strain broadenings as higher doublets become populated.

The Tm^{3+} ions have excited singlets as well as doublets. As these become thermally populated, there are fewer ions in the ground doublet, so the details of the random-type strains should change, as should the energy C_2. Effects due these singlets seem not to have been considered before, but

as far as the EPR results are concerned they do not seem to be important.

Our discussion has been given in the context of zero applied magnetic field. But to observe the Gd^{3+} resonances a magnetic field has to be applied, and this, of course, also acts on the Tm^{3+} ions. For an isolated doublet $g_\perp = 0$,[7] and it is therefore convenient to assume that the field is applied along the c axis, x. Then the term $\mu_B g_\parallel H \times \sum_n S_x^{(n)}$ is added to the Hamiltonian $\mathcal{H}_{Tm}$. We now have a term which does not commute with the rest of the Hamiltonian, so in a sense there is a competition between what the coupling to the lattice wants to do and what the coupling to the magnetic field wants to do. Experiments[8] on $TmVO_4$ show that the distortions near T_c can be affected by an applied magnetic field, but they suggest that, for fields of strengths used in our experiments, these effects are small. Some care is needed here, for each Tm^{3+} is in an environment of low symmetry, because of the random strains, so it does not have a lowest doublet (since this will be split) and in zero field the two components of the doublet are each nonmagnetic. This is so, even though $g_\parallel$ for the true doublet is large.[7] The effect of an applied magnetic field will be to induce a moment, so that locally an effective Hamiltonian for each Tm^{3+} will be[1]

$$\mathcal{H}_{local} = \mu_B g_\parallel H S_x + \Delta S_z. \quad (4)$$

We therefore have another effect—that even though the doublet appears to be magnetic it may in fact be only weakly so in the fields used. In $TmVO_4$ the upper doublet is probably less magnetic than the lower doublet, and this may be important since the observed spectrum depends not only on the zero-field splittings but also on the line-broadening mechanisms, such as the dipolar interactions between neighbors. If in fact the Tm^{3+} ions are only weakly magnetic, then the dipolar linewidth will be small.

In conclusion, much of the previous work has concentrated on what happens at and below the phase transition. In all previous work, there is no emphasis that above T_c the Jahn-Teller coupling can give rise to random strains in this system.[9] In fact, there should be a number of interesting phenomena to be observed above the phase transition, associated with the random strains and the quenching of magnetic moments. In this Letter, we have suggested that the peculiar temperature variation of the EPR linewidths in $TmVO_4$(Gd) may be an example of such phenomena. Further theoretical and experimental work is clearly needed to establish the relative importance of random strain and dipolar effects and their interdependence.

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