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Powder EPR study of the Jahn-Teller effect and phase transition in Cu^{2+}:$ZnTiF_6 \cdot 6H_2O$

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A powder electron-paramagnetic-resonance study of Cu^{2+} in $ZnTiF_6 \cdot 6H_2O$ has been made at 35 GHz in the range 4.2—300 K. The low-temperature structure has been related to four single-crystal Jahn-Teller transitions. The single-line spectrum at high temperature was replaced gradually by a multiline spectrum at temperatures below 165 K, i.e., about 6 K below the single-crystal transition temperature for 0.043 at. % Cu^{2+} concentration. The exponential line broadening with temperature in the high-temperature region (above phase transition) was fitted to an Orbach process, with an excited state at 1350 cm^{-1}. A Jahn-Teller stabilization energy $E_{JT} = 1000$ cm^{-1} may be obtained from this fit. The relaxation rate $1/T_1$ is deduced and compared with that for Cu^{2+}:$La_3Mg_2(NO_3)_{12} \cdot 24H_2O$.

INTRODUCTION

Recently interesting EPR results have been obtained with Cu^{2+} doped in several host lattices, e.g., $CoSiF_6 \cdot 6H_20$,[1] $FeSiF_6 \cdot 6H_20$,[1] and $ZnTiF_6 \cdot 6H_20$.[2] These crystals exhibit structural transitions. $ZnTiF_6 \cdot 6H_2O$ (ZNTFH) appears to be isomorphous with $MgSiF_6 \cdot 6H_2O$ (Ref. 3) and $FeSiF_6 \cdot 6H_2O$, (Ref. 4) which have two inequivalent ions related by a mirror plane containing the symmetry axis. On cooling there is a phase transition from the trigonal space group $D_{3d}^5(R\bar{3}m)$ to the monoclinic group[3] $D_{2h}^5(P2_1/C)$.

^{19}F NMR studies[5] reveal a first-order phase transition at 182 K (T_{c1}) when the rotation of the fluorine octahedra stops and the single ^{19}F line splits into two, indicating the loss of a chemical equivalence between the fluorine atoms following a tetragonal distortion of the $(TiF_6)^{2-}$ octahedra. Chowdhuri *et al.*[6] found a second weak transition of a continuous nature in ZNTFH at 217 K. The latter transition is found to occur at 230 K in ZNTFD,[7] where T_{c1} remains unaffected on deuteration. In the low-temperature monoclinic phase, EPR measurements on Ni^{2+}: $ZnTiF_6 \cdot 6H_2O$ have indicated the presence of six inequivalent magnetic sites, with spectra coinciding along the pseudotrigonal *c* axis.[8] Perpendicular to the *c* axis, these spectra reduce to two sets of three lines, each set showing a 60° rotational symmetry. As a result, the *z* axis of the six inequivalent spectra of non—Jahn-Teller ions such as Ni^{2+} and Fe^{2+} lie within a few degrees of the crystal *c* axis. The Cu^{2+} ion in each of these systems at high temperature is embedded in a site symmetry of a trigonally distorted water octahedron ($R\bar{3}m$). The trigonal distortion of the water octahedron cannot lift the degeneracy of the orbital ^2E ground state of the Cu^{2+} ion and consequently the Cu^{2+} ion in such systems is a Jahn-Teller (JT) ion.[9]

Hock and Thomas[10] showed theoretically that a JT ion can couple to the soft mode of the structural transition in addition to the local vibrational mode of E_g symmetry. As a result one obtains a weak to strong temperature-dependent enhancement of the local JT effect as the critical temperature T_c is approached from above. In other words the JT effect is expected to be considerably modified in such lattices in comparison to those without structural transitions, e.g., $ZnSiF_6 \cdot 6H_2O$,[11] CaO,[12] SrO,[13] $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$,[14] etc. Our recent extensive EPR studies in single crystal of Cu^{2+}: $ZnTiF_6 \cdot 6H_2O$ in the temperature range 350—1.5 K have shown an enhanced JT effect[2] in the sense that three axially symmetric anisotropic spectra corresponding to each of the two inequivalent JT Cu^{2+} ions were observed at temperatures much higher than those in the above systems. The gradual change in the Cu^{2+} EPR spectrum over a wide range of temperature found in single crystal ZNTFH was not present in JT systems of higher symmetry such as $ZnSiF_6 \cdot 6H_2O$, $Ca(OH)_2$, NaCl, etc. The presence of a weak monoclinic symmetry in ZNTFH below T_c makes the potential wells corresponding to the three distorted configuration of the water octahedron energetically inequivalent[2] (by ~ 100 cm^{-1}).

Another interesting observation that has been made through the single-crystal EPR study is the modification of the structural transition by the JT effect. The transition temperature T_c of the host lattice was lowered[1,2,15] by increasing the concentrations of the Cu^{2+} or Ni^{2+}. With Cu^{2+} the decrease in T_c was much larger than that for Ni^{2+}.

The change in the EPR signal (in the high temperature phase) is sharp and discontinuous around T_c for low Cu^{2+} concentrations, while the change takes place over a large temperature range and is not discontinuous around T_c for high Cu^{2+} concentrations.[15] Recently, the influence of JT impurities in a ferroelectric phase transition has been theoretically considered by Vikhnin.[16].

This paper concerns with powder EPR studies of Cu^{2+}:$ZnTiF_6 \cdot 6H_2O$. We find that though the powder spectrum is different from that of a system with axial spin Hamiltonian parameters, nature of Jahn-Teller effect (static or dynamic) can be established through the powder studies. The transition temperature is found to be lowered in powdered material in comparison to the single crystal. The temperature variation of line width above T_c is due to relaxation via an Orbach level at 1350±50cm^{-1} above the ground ^2E vibronic state.

EXPERIMENT

Single crystals of ZNTFH were grown by slow evaporation of an aqueous solution of $ZnTiF_6$ obtained by dissolving $ZnCO_3$ in 40 vol.% H_2TiF_6. Small amounts of $CuCO_3$ were added to grow the doped crystals. Only good single crystals having uniform Cu^{2+} concentration were chosen for EPR studies. For powder studies the crystals were ground thoroughly and sealed in spectroscopically pure quartz capsules. The same crystals were used for both the powder and single crystal studies and were analyzed by Galbraith Chemical Laboratories, USA, for estimation of the Cu^{2+} concentration. EPR spectra were measured over the temperature range 360—1.5 K with a Q band (33—35 GHz) reflectance spectrometer. Temperatures between 360 and 77 K were varied by a manual temperature control. An approximately uniform cooling and heating rate of 1 °C/min to 1 °C/100 min could be attained. The sample could be maintained at any temperature above 77 K constant within ±0.1 °C for 20 min. The temperature of the sample structure was measured by both E-and T-type thermocouples. The thermometers and the digital readouts were calibrated at temperatures of liquid N_2, solid CO_2, a toluene and liquid-N_2 slush, and a mixture of isopropane and solid CO_2. At 4.2 K and below, a purely static JT effect[2] was observed from the two inequivalent Cu^{2+} ions in single crystal Cu:ZNTFH. At 77 K also a nearly static Jahn-Teller effect characterized by three axially symmetric EPR spectra (corresponding to the water octahedron distorted along x,y,z axes) due to each of the two inequivalent JT Cu^{2+} ions in the unit cell was observed. The principal g values $g_{\parallel}=2.43$ and $g_{\perp}=2.12$ at 77 K were close to the corresponding values at 4.2 K.

In Figs. 1 and 2 the powder EPR spectra of Cu:ZNTFH at 77 and 4.2 K are shown. (Above the transition temperature T_c the powder EPR spectrum is identical to the isotropic single crystal spectrum with $g=2.223$.) At 77 and 4.2 K four distinct lines are observed. Only at 4.2 K and below, are four evenly spaced, well resolved hyperfine lines (for Cu, $I=\frac{3}{2}$) observed at the lowest field (see Fig. 2). The mean hyperfine separation is found to be 90±5G, quite consistent with $A_{\parallel}(92\pm3$ G), obtained from single-crystal measurements.[2] No hyperfine lines are seen at the highest field ($g_{\perp}$) in contrast to that in the single crystal.[2] The center of the four hyperfine lines corresponds to $g_{\parallel}=2.47\pm0.01$, in good agreement with single-crystal measurements.[2] Partially resolved hyperfine lines are also seen in the middle two lines at 4.2 K. At 77 K, unlike the single crystal, no hyperfine structures are seen in the powder, and all the four lines are broadened because of the unresolved hyperfine lines. (Of course spin lattice relaxation also adds to the broadening.)

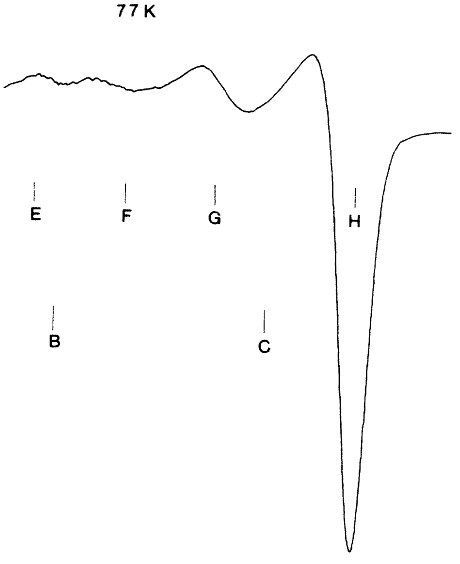

FIG. 1. EPR spectrum of powdered Cu^{2+}:$ZnTiF_6\cdot6H_2O$ at 77 K. $\nu=34.115$ GHz. The markers B and C correspond to 9.808 and 10.815 kG, respectively. The markers E, F, G, and H correspond to single-crystal EPR transitions (see text).

The centers of the powder lines observed at 77 and 4.2 K (see Figs. 1 and 2) correspond fairly well to the following single-crystal transitions.

(i) $g_{\parallel}$ and $g_{\perp}$ shown by the vertical lines E and H, respectively, in Figs. 1 and 2.

(ii) $g_{[111]}$ shown by the vertical line G.

(iii) Lowest field transition in the plane perpendicular to the c axis. This is shown by vertical line F. If this interpretation is correct, then the g values corresponding to the lines F and G are related to $g_{\parallel},g_{\perp}$ by the relations

$$g_2^2=(2g_{\parallel}^2+g_{\perp}^2)/3\ , \tag{1}$$

$$g_3^2=(g_{\parallel}^2+2_{g\perp}^2)/3\ , \tag{2}$$

assuming a perfect octahedron of water surrounding each

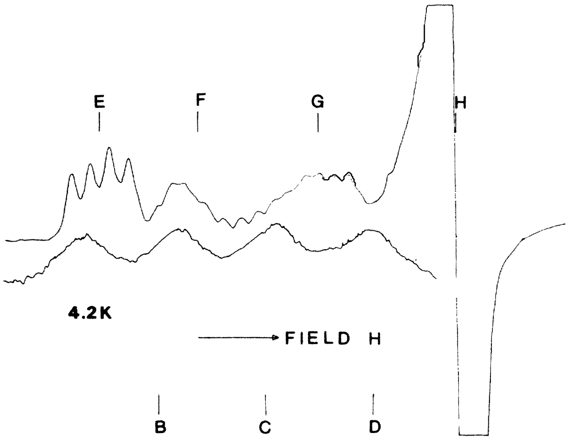

FIG. 2. Q-band EPR spectrum of powdered Cu^{2+}:$ZnTiF_6\cdot6H_2O$ at 4.2 K; $\nu=33.69$ GHz. The markers B, C, and D correspond to 10.010, 10.513, and 11.015 kG, respectively. The markers E, F, G, and H correspond to single-crystal transitions at 4.2 K (see text). The lower spectrum corresponds to the lowest field four hyperfine lines with $B=9.657$, $C=9.758$, and $D=9.859$ kG.

Cu^{2+} ion in ZNTFH. The reasons why lines F and G would appear in the powder spectrum are under investigation. It may be mentioned that the high-temperature g value is also given by Eq. (2). The powder EPR transitions corresponding to both [100] and [111] type of axes have thus been observed for the first time in ZNTFH. In the single crystal we observed that both the EPR signals at the lowest field ($g_{\parallel}$) and at the highest field ($g_{\perp}$) positions move to lower and higher fields, respectively, as the sample is cooled below the phase transition temperature T_c down to 4.2 K. Below 4.2 K there was no shift of either extreme line. Similar observations have been made through the powder EPR studies although the signals were not always sharp like those of the single crystal. In single-crystal ZNTFH resolved hyperfine lines appeared at 125 K along the [100] direction. With lowering of temperature the hyperfine splittings ($A_{\parallel}$ and $A_{\perp}$) increased down to 4.2 K.

It may be mentioned that we have also measured powder EPR spectra on $Cu{:}ZnSiF_6{\cdot}6H_2O$, a well-known JT system at 300, 77, 4.2, and 2.2 K. Only one EPR signal devoid of any hyperfine structure was observed between 300—77 K with $g=2.22$. The following two transitions ($g_{\parallel}, g_{\perp}$) were observed at 4.2 K and below.

(i) One of these consisted of four evently spaced hyperfine lines with average splitting 93±5 G. The lines were centered around $g_{\parallel}=2.46\pm0.01$ in agreement with the single-crystal measurements.[11]

(ii) The other was an intense perpendicular line with $g_{\perp}=2.10$ without any hyperfine line in contrast to that in the single crystal. The observations of the two intermediate lines in ZNTFH might be related to the two inequivalent JT ions in the unit cell.[2] Similar results have also been observed in Cu:ZNTFD. Both in ZNTFH and $ZnSiF_6{\cdot}6H_2O$ a single high-temperature g value (for powdered samples) is found to be related with $g_{\parallel}$ and $g_{\perp}$ values at 4.2 K through Eq. (2).

STRUCTURAL TRANSITION THROUGH POWDER EPR IN $Cu{:}ZnTiF_6{\cdot}6H_2O$

We have recorded the phase transition in powders of Cu:ZNTFH through EPR. The characteristic features of the transition are found to be somewhat different from that of the single crystal. In powder the high temperature EPR signal intensity decreases over a range of temperature around T_c. Below T_c, an anisotropic spectrum appears on the low and high field sides of the isotropic high-temperature spectrum (HTS). HTS almost disappears within a few degrees below T_c. However, about 20 °C below T_c an EPR transition appears at the same position as HTS. Unlike the single crystal, the corresponding signal intensity increases with decrease of temperature. The corresponding g value is independent of temperature, whereas the low and high field lines shift to lower and higher fields as the temperature is lowered to 4.2 K. In pure ZNTFH (without Cu^{2+} ions) the transition occurs at 182 K and is accompanied by latent heat of transition. In the single crystal, the isotropic signal splits into several components (as many as six) at $T_c\pm1$ °C in all directions except along the [111], where no structural transition can be recorded through EPR. T_c in the powder is recorded as the temperature at which a significant loss and gain in intensity of the isotropic EPR signal is noticed first while cooling and then while warming at an approximate rate of 1°C/15 min. These for a dilute single crystal and its powder are given in Table I for a sample of copper concentration 0.2 at. %. The reasons for lowering of transition temperature with powdering are under investigation.

TABLE I. Transition temperatures T_c.

	T_c (K)	
	Cooling	Warming
Single crystal	171±0.5	171.6±0.5
Powder	165±2	167±2

LINEWIDTH

The peak-to-peak derivative EPR linewidth $\Delta H_{\text{p.p.}}$ in the powdered specimen varies exponentially with temperature as shown in Fig. 3. This is equal to the single-crystal linewidth within experimental error. Exponential line broadening has also been observed in the following powdered specimens (see Refs. 1 and 17):

$Cu^{2+}{:}CoSiF_6{\cdot}6H_2O$, $Cu^{2+}{:}FeSiF_6{\cdot}6H_2O$,

$Ni^{3+}{:}Al_2O_3$, $Ni^{3+}{:}SrTiO_3$,

$Pt^{3+}{:}Al_2O_3$.

$\Delta H_{\text{p.p.}}$ in Cu^{2+}:ZNTFH in the temperature range 180—330 K was found to be independent of Cu^{2+} concentration up to 7 at. %. This shows negligible dipolar contribution[18] to the linewidth broadening in the dilute sample (0.2 at. %Cu). The line broadening is caused by the spin-lattice relaxation rate $1/T_1$, which for JT ions is much faster than for non-JT ions and is strongly temperature dependent.[9,11,14] Following Williams *et al.*[19] and Ham[9]

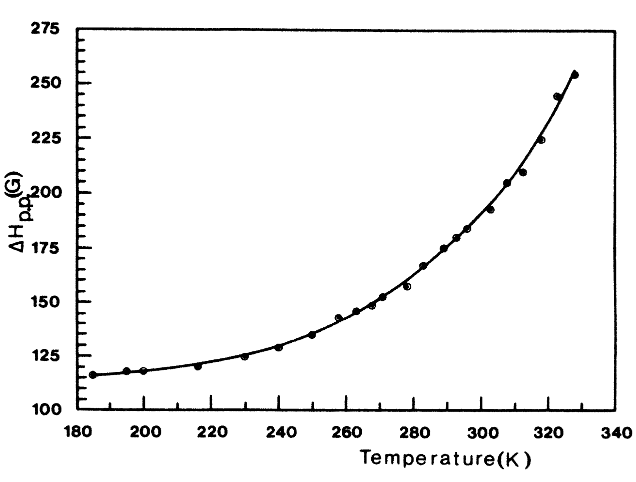

FIG. 3. Peak-to-peak EPR derivative linewidth ($\Delta H_{\text{p.p.}}$) in $Cu{:}ZnTiF_6{\cdot}6H_2O$ above the phase transition temperature T_C (171 K). Circles represent observed values (maximum error is ±8 G). The solid line indicates those calculated from Eq. (5).

$$1/T_1 = aT + bT^3 + cT^5 + d\exp(-\Delta_1/k_B T)\ , \quad (3)$$

where the term linear in T arises due to one-phonon direct process and is important only at very low temperatures. The terms bT^3 and cT^5 are due to two-phonon nonresonant relaxation. The T^3 term arises due to reorientation of the JT ion without spin flip; T^5 term takes into account the spin flip in the reorientation. The fourth term is due to two-phonon resonant process also known as Orbach process via real excited level at Δ_1. Δ_1 is the separation between the ground state ^2E and an excited vibronic level.

The linewidth can then be expressed by

$$\Delta H_{\text{p.p.}} = A_0 + AT^3 + BT^5 + D\exp(-\Delta_1/k_B T)\ . \quad (4)$$

A_0 being the residual linewidth arising out of unresolved hyperfine interactions, we assume that it is temperature independent in the interval 330—185 K. [Temperature-dependent g and A terms were observed only below the structural transition (171 K).] The constants A, B, C, etc. are related to a, b, c, etc. in Eq. (3) by $A = \dfrac{2h}{g\mu_B} a \cdots$. We attempted to obtain a least-square fit of the observed linewidths with the various possible combinations of the different terms in Eq. (4) and found that the following Eq. provided the best fit (Fig. 3).

$$\Delta H_{\text{p.p.}} = 115 + 0.49\times 10^5 \exp[(-1350\ \text{cm}^{-1})/k_B T]\ , \quad (5)$$

i.e., giving a value of $\Delta_1 = 1350 \pm 50\text{cm}^{-1}$ for the excited vibronic level above the state ($^2A_2$ or $^2A_1$) from which the isotropic spectrum is arising or above the ^2E ground state if the isotropic signal is arising out of rapid phonon induced reorientation of the Cu^{2+} ion among the different distorted configurations. Similar values of Δ_1 have been observed in the JT system Ni^{3+} in Al_2O_3. Inclusion of terms $\sum_{n=0}^{N} AnT^n$, in general (N is an integer varied from 0 to 10), with and without the exponential term in Eq. (4), did not provide a better fit. Some of the coefficients were always negative. This is unacceptable on the grounds that the corresponding contribution to the spin-lattice relaxation rate should have a positive temperature coefficient. Moreover the value of $y = \sum_i (\Delta H_{\text{obs}} - \Delta H_{\text{calc}})_i^2$ was always larger than that observed from Eq. (5). In the range 180—325 K the second term makes the dominant contribution to the spin-lattice relaxation rate ($1/T_1$) which, with the help of Eqs. (3) and (5) and the relation $D = 2hd/g\mu_B$, could be given by

$$1/T_1 = (5\pm 1)r \times 10^{11} \exp[(-1350\ \text{cm}^{-1})/k_B T)]\ , \quad (6)$$

where r is a factor of the order of unity which depends on the line shape. The line shapes of the derivative EPR spectrum were analyzed[20] at two temperatures, 300 and 180 K. The lines were found to be closer to Gaussian than Lorentzian (the $\Delta H_{1/2}/\Delta H_{\text{p.p.}}$ ratio varies between 1.28 and 1.35). Using the expression of Soos *et al.*[21] for the contribution of the unresolved hyperfine interaction to the second moment of the residual linewidth ($\sim 115 \pm 5$ G) we obtain the average value of

$$\langle (A_{\parallel}^2 g_{\perp}^2 \cos^2\theta + A_{\perp}^2 g_{\parallel}^2 \sin^2\theta)/g^2 \rangle^{1/2} = 59\text{G}$$

which is in good agreement with the single-crystal static A value (63 G) along a [111] direction. High-temperature $1/T_1$ rates are available only in the JT system Cu:$La_2Mg_3(NO_3)_{12}\cdot 24H_2O$ (LMN) where the value of Δ_1 (Ref. 19) is 200 cm^{-1} and the $1/T_1$ rate at a temperature, say 250 K, is about 16 times larger than that in Cu:$ZnTiF_6\cdot 6H_2O$. A faster $1/T_1$ rate also signifies a faster $1/\tau$ rate[9] (reorientation rate among the three JT distorted configurations) which averages out the anisotropic spectra at high temperature. In Cu:LMN, Cu:$Zn(BrO_3)_2\cdot 6H_2O$, where no structural transitions are reported so far, the anisotropic EPR signal is not observed until at quite low temperatures, unlike in Cu:ZNTFH, where immediately below T_c anisotropic signals are observed and three axially symmetric EPR spectra due to each of the two inequivalent Cu^{2+} ions are clearly observed at 77 K.

A few words might be said about the nature of the excited level at $\cong 1350\ \text{cm}^{-1}$ in Cu:ZNTFH through which the high-temperature Orbach relaxation process takes place for the Cu^{2+} ion. The ^2E orbitally degenerate level of the Cu^{2+} ion after linear JT coupling with the ^2E_g type ligand vibrations split into the following levels:[9,11,13] ^2E (doublet); $^2A_1$, $^2A_2$ (degenerate). Quadratic coupling or warping gives rise to the splitting between $^2A_1$ and $^2A_2$ and the strains of the lattice split ^2E. For $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$, $^2A_2$ lies lower than $^2A_1$ (Ref. 13) and the high-temperature isotropic signal might be due to the population of $^2A_2$. It might as well be due to phonon induced reorientation of the Cu^{2+} ion among the different distorted configurations. O'Brien[22] has calculated the different energy levels as a function of $2\beta/2\alpha$(2β denotes the barrier height separating the adjacent wells and 2α is the kinetic energy of the ion). β/α is expected to be temperature dependent so that at low temperature it becomes very large compared to that at high temperature. For large β/α the first excited singlet $^2A_2$ approaches ^2E while $^2A_1$ recedes away from ^2E vibronic doublet and one obtains the condition of a static JT regime.[9,23]

The values $\Delta E(^2A_2\text{-}^2E) = 0.3\ \text{cm}^{-1}$ and $\Delta E(^2A_1\text{-}^2E) = 200\ \text{cm}^{-1}$ have been obtained for Cu:LMN in the static JT regime (below 20 K). However, at high temperature the separation $^2A_2$-^2E could be expected to be somewhat larger than 0.3 cm^{-1}, $^2A_2$-^2E is expected to be less than 200 cm^{-1}. Thus the Orbach relaxation in the high-temperature EPR transition in Cu:ZNTFH may not be occuring via the first excited level $^2A_2$ or $^2A_1$, it may possibly be occuring through one of the much higher excited states.[21,23]

It may be mentioned that Hoffman and Estle[23] following the multistep matrix formulation method calculated the energy levels for a JT ion with orbital ground state considering one mode intermediate coupling. For the first three energy levels ^2E, $^2A_1$, and $^2A_2$ results are identical to those obtained earlier.[9,22] For the strong linear coupling limit their calculations agree with those of O'Brien for the lowest 20 states with $\beta/\alpha < 100\ \text{cm}^{-1}$. These energy levels are within $(0\text{—}2)\hbar\omega$ above the ground state. In the intermediate coupling range the energies of the states lying more than $\hbar\omega$ above the ground state vary with β/α in a manner quite unlike any level obtained in the strong coupling approximation. It might appear that these energy levels should take part in Orbach relaxation. For the least-square fit of the linewidth data Δ_1 in Eqs. (4) and (5) was varied between 0–3000 cm^{-1} at steps of 20 cm^{-1} and the level at $\Delta_1 = 1350 \pm 50$ cm^{-1} provided the best fit. Debye temperature Θ_D in ZNTFH may be assumed to be ~ 100 K as obtained in $ZnSiF_6 \cdot 6H_2O$. $\hbar\omega$ would be of the order of 50 cm^{-1}, and any energy level within $(0-10)\hbar\omega$ provides much different rates of temperature variation of linewidth than is observed in Cu:ZNTFH.

For Orbach relaxation to take place, the energy level Δ_1 should lie within the phonon spectrum of the lattice. However, a number of systems[17] such as Ni^{3+} in Al_2O_3, $SrTiO_3$, and Pt^{3+} in Al_2O_3 exponential EPR line broadening has been observed. In these systems Δ_1 is higher or comparable to the highest lattice mode energy.

In this connection it may be recalled that Slonzcewsky[24] demonstrated the existence of an elastically and centrifugally stabilized mode (at the upper potential branch of the ^2E ion) which may occur well above the maximum frequency or vibration of the host lattice. Following Slonzcewsky, Muller[25] used the equation

$$\Delta_1 = \varepsilon[2.0 + \tfrac{9}{8}(\varepsilon / K_B \Theta_D)^2] ,$$

where ϵ is related to the JT stabilization energy $E_{JT} = \varepsilon^3 / 2\hbar^2\omega^2$. He obtained $E_{JT} = 760$ cm^{-1} for Ni^{3+} in Al_2O_3 with $k_B\Theta_D = 300$ cm^{-1} and $\Delta_1 = 1530$ cm^{-1}. Thus $E_{JT}/\hbar\omega = 3.8$. A ratio of $E_{JT}/\hbar\omega > 5$ would be necessary to observe a static JT effect according to Ham.[9] In fact the Ni^{3+} ion in the oxide environments Al_2O_3 and $SrTiO_3$ (Ref. 26) shows a dynamic JT effect in agreement with Ham's criterion. (A tunneling splitting of $3\Gamma = 55$ cm^{-1} was deduced from thermally detected ESR.)[26] In the case of Cu:ZNTFH if we use $\Theta_D = 95$ K as obtained[27] in $ZNSiF_6 \cdot 6H_2O$, from Eq. (6) we obtain $E_{JT} = 1000$ cm^{-1}. Using $\hbar\omega \sim \frac{2}{3} k_B \Theta_D$ (Ref. 28) we find that $E_{JT}/\hbar\omega = 22$. Though this ratio may not be taken as exact because Θ_D might differ from that of $ZnSiF_6 \cdot 6H_2O$, it should be noted that a static JT effect with the Ham reduction factor $q = 0.5$ has been observed in Cu:ZNTFH earlier.[2]

CONCLUSIONS

The experiments indicate the following.

(1) Powder EPR spectra of a crystal containing two inequivalent Jahn-Teller paramagnetic ions can show transitions parallel and perpendicular to [111] and [100] axes.

(2) The phase transition temperature of such materials is decreased when powdered.

(3) The static or dynamic nature of Jahn-Teller effect can be established through studies of temperature variation of EPR linewidths in powdered material.

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