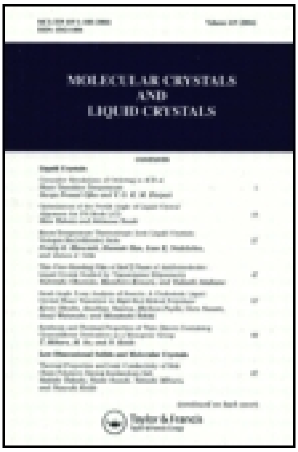

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Phase Transition Induced Motional Averaging of Hyperfine Interaction of Transition Metal Complexes in Molecular Solids

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Phase Transition Induced Motional Averaging of Hyperfine Interaction of Transition Metal Complexes in Molecular Solids

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A reduction of the anisotropic hyperfine interaction of dopant transition metal complexes due to motional averaging is observed during order-disorder phase transitions in molecular solids. The onset of the reduction of the hyperfine splitting of copper benzoyl acetonate doped into hexamethyl benzene and cyclohexane corresponds to temperatures at which other data show evidence for order-disorder phase transitions. It is shown that this effect can be used to study the dynamics of the disordering. The approach is used to present evidence for the existence of new order-disorder phase transitions above room temperature in ammonium dihydrogen phosphate and potassium dihydrogen phosphate. Evidence for molecular tumbling is also found in the solid state of the liquid crystal material *p*-methoxy cinnamic acid.

INTRODUCTION

When a paramagnetic molecule or complex undergoes slow tumbling with a characteristic frequency in the order of the anisotropic hyperfine splitting, the anisotropic hyperfine interaction is motionally averaged. The onset of this averaging is manifested in the electron paramagnetic resonance (EPR) spectrum as an inward shift of the extrema resonance of the spectrum and an increase in the line width. The reduction of the hyperfine splitting can be used to study dynamical behavior in the condensed phase if the relationship of the changes in the spectrum to the correlation time of the motion are known. Theoretical models have been developed to account for the changes in the EPR spectrum of the $S = 1/2$ and $I = 1$ nitroxide molecules.[1,2] However these models have limited applicability because they require an a priori knowledge of the motionally narrowed line width and because the theories only apply to $I = 1$ systems. Because of this and small changes observed, nitroxide molecules have not been widely used to study motional effects in solids. Of considerably more promise are species with large anisotropic hyperfine interactions. For the case of an axially symmetric hyperfine tensor, the upper limit of of the correlation time, τ, of the motion that an EPR spectrum will be sensitive to is given by[3]:

$$\tau = (8/3)\, T_2^2(A_\parallel - A_\perp)^2 \tag{1}$$

where $A_\parallel$ is the parallel component of the hyperfine tensor, $A_\perp$ the perpendicular component and T_2 the spin-lattice relaxation time. A more anisotropic hyperfine tensor which has a larger anisotropic hyperfine interaction will thus be more sensitive to motional effects. Similarly a more anisotropic g tensor will contribute.[4] Thus a good paramagnetic probe to sense motional effects in a lattice will be a transition metal complex such as copper benzoyl acetonate (CuB) which has a quite anisotropic g and A tensor.

Recently theoretical models applicable to EPR spectra of transition metal complexes systems with $I > 1/2$ have been developed which relate the changes in the spectra to the correlation time. The predictions of these models are quantitatively simple and do not require an a priori knowledge of the motionally narrowed line width.[5,6,7]

There has been no effort to use motional averaging of hyperfine splitting of transition metal complexes to study dynamical effects in solid phase transitions. Most structural phase transitions in solids involve some form of motion of the subunits of the lattice. Of interest here are order-disorder transitions in molecular solids in which the molecules acquire additional degrees of rotational freedom ranging from limited rotation about an axis to full rotation. The purpose of this work is to determine whether the onset of order-disorder motion in a lattice can induce an averaging of the hyperfine splitting of transition metal complexes doped into the solid and if this can be used to obtain dynamical information about the disordering process. The results are compared when available with other spectroscopies which measure motion of the intrinsic molecules of the lattice such as temperature dependent nuclear magnetic resonance spin-lattice relaxation times. The approach is used here to study the crystal to librator transition in cyclohexane and order-disorder motion in crystalline hexamethylbenzene (HMB) both of which have been studied by other spectroscopies allowing a comparison with the EPR data. In these two materials motional effects are observed in the EPR of the dopants in the same temperature region where other data indicate fluctuations. Studies have also been made on systems for which there is little or no evidence of phase transitions or motion in the solid and evidence is obtained for dynamical behavior not previously observed. Motional effects are observed in the solid phase of the doped nematic liquid crystal *p*-methoxy cinnamic acid (PMCA) prior to the transition to the liquid crystal phase. Evidence is also presented for fluctuations suggestive of phase transitions above room temperature in ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP). In the latter the effects of the EPR of the dopant were observed in a temperature region where a phase transition has been reported to exist but about which there is little information.

EXPERIMENTAL

Cyclohexane, HMB and PMCA were doped by cooling the materials from their liquid phase in which was dissolved copper benzoyl acetonate. ADP and KDP were doped by slow evaporation of solutions of ADP and KDP containing trace amounts of $VOSO_4$. The crystalline material was ground into find powders. EPR studies were made using a Varian E-9 spectrometer operating at 9.2 GHz. The temperature of the sample was controlled in the cavity using a Varian 4540 nitrogen gas flow controller allowing a control of the temperature to ±1°C. The sample temperature was monitored by a small thermocouple in contact with the sample.

RESULTS

(a) Method

The separation between the lines of an EPR spectrum of a species in a single crystal depend on the orientation of the dc magnetic field with respect to the symmetry axis of the paramagnetic complex. These splittings are determined by the anisotropic dipolar and contact hyperfine interaction. Thus for a paramagnetic species fixed in direction in a single crystal the separation between the lines will vary with the orientation of the dc magnetic field. In an amorphous material or fine powder the symmetry axis of the species have all possible orientations with respect to the magnetic field and the EPR spectrum is then essentially a superposition of spectra from each orientation. Such spectra for simple systems can be interpreted by computer simulation techniques and the spin Hamiltonian parameters obtained directly from the spectra. Figure 1(a) shows the powder spectrum of CuB in HMB which has been ground into fine powders. The powder spectra of copper complexes have been studied by computer simulation techniques and are well understood.[5] The peaks in the spectrum occur at magnetic field values that correspond to the magnetic field values at the extrema positions of the angular variation data in the single crystals. The four low field peaks are the extrema arising from the parallel components of the axial hyperfine tensor from the interaction of the unpaired electron with the $I = 3/2$ nucleus of copper. The separation of these low field lines is a measure of $A_{\parallel}$, the parallel component of the hyperfine tensor. Figure 1(b) shows the spectrum obtained when HMB is heated above the melting temperature to the liquid phase. The spectrum consists of four lines equally separated

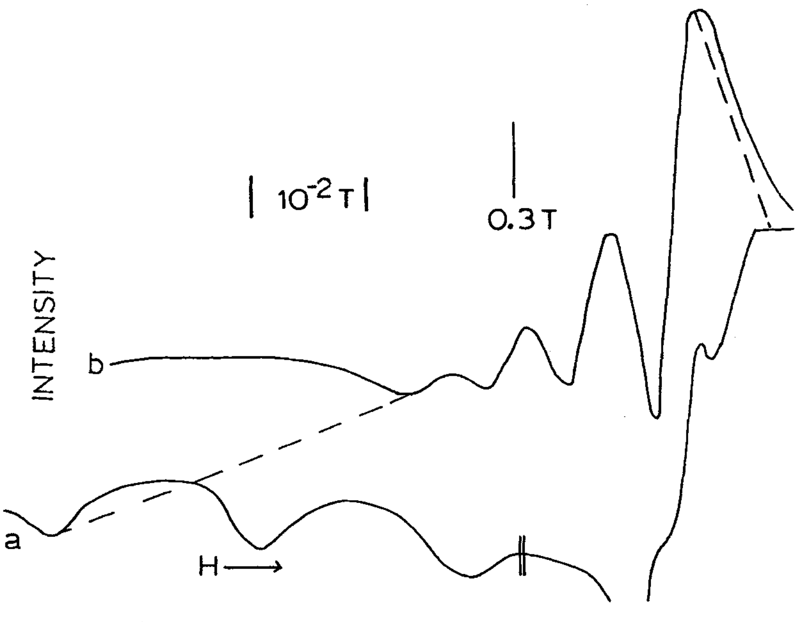

FIGURE 1 (a) The EPR spectrum of CuB in powders of hexamethyl benzene. The spectrometer gain on the left side of the double dashed line is a factor of ten larger than the right. (b) EPR spectrum of CuB in melted liquid hexamethyl benzene where anisotropic hyperfine splitting has been averaged to zero because of tumbling.

from their adjacent lines. In this spectrum the dipolar anisotropic hyperfine interaction has been averaged to zero because the CuB complex is rotating with a correlation time less than 10^{-10} seconds. The splitting between the lines in the liquid phase is the isotropic Fermi contact interaction. In effect because the complex is moving the outer lines of the spectrum of the fixed system have coalesced (shown by the dashed line). In some types of phase transitions, the transition between the stationary state and the tumbling state is sufficiently gradual with temperature that the inward shift of the outer lines of the powder spectrum can be measured as a function of temperature and information about the dynamical processes of the phase transition obtained. This is the essence of using motional averaging of hyperfine splitting to measure dynamical behavior in the solid state. Recent theoretical modeling of the effect of slow tumbling on EPR spectra, which relates the changes in the spectrum to the correlation time of the motion, makes this possible. It has been shown that as the correlation time of the motion of the paramagnetic probe decreases from 10^{-7} s to 10^{-10} s the outer lines of the spectrum shift inward and this shift depends on the correlation time as $\tau^{-1/2}$.[6,7] The onset of slow tumbling is also manifested in the spectrum by a broadening of the lines. The theory shows that the net motional line width also depends on the correlation time as $\tau^{-1/2}$.[6,7] The net motional line width can be obtained from the difference between high field and low field widths of the parallel edge extrema spectrum. In the case of the powder spectrum of CuB the high field line of the parallel edge spectrum is not resolved because it overlaps the lines from the perpendicular edge spectrum and thus the motional line width can not be obtained.

(b) Hexamethyl Benzene

Hexamethyl benzene (HMB) has a triclinic unit cell at room temperature containing one molecule which lies in the *ab* plane.[8] At 383 K the structure undergoes a phase transition to an orthorhombic structure. It has been suggested that the onset of a rotation of the HMB molecule is involved in this transition.[9] The transition has been studied by a number of spectroscopic techniques.[9,10,11] Temperature dependent NMR studies have shown a marked increase in the spin-lattice relaxation time through the transition temperature which has been attributed to the onset of a rotation of the HMB molecule about its C_6 axis.[10] When powders of HMB doped with CuB are heated above room temperature a gradual inward shift of the low field extrema of the spectrum is observed indicative of the onset of motion of the CuB in the lattice. Figure 2 shows a plot of the inward shift, Δ, of the extrema versus temperature. Since the theory predicts the shift should depend on the correlation time as $\tau^{-1/2}$, the log of the reciprocal of the square of the shift is plotted versus the reciprocal of the absolute temperature. The data shown in Figure 3 can be fitted to a straight line indicating thermally activated Arrhenius kinetics. The fit yields a barrier to rotation for the CuB of 0.92 eV. It is likely that the onset of motion of the HMB molecules is responsible for the motion of the probe CuB although the details of the kinetics of the CuB motion may not be the same as that of the HMB molecules. A study of the temperature dependence of the NMR spin-lattice relaxation time has indicated the HMB motion to follow Arrhenius kinetics having a barrier to motion of 0.21 eV. lower than that of the CuB.[10]

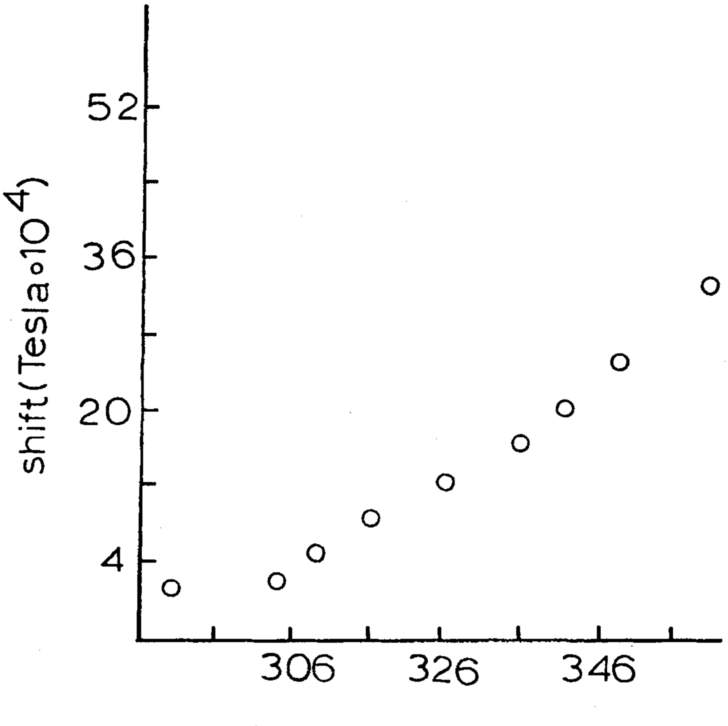

FIGURE 2 Inward shift of the low field extrema of the EPR powder spectrum of CuB in hexamethyl benezene as a function of temperature in the solid phase through the 383 K order-disorder phase transition.

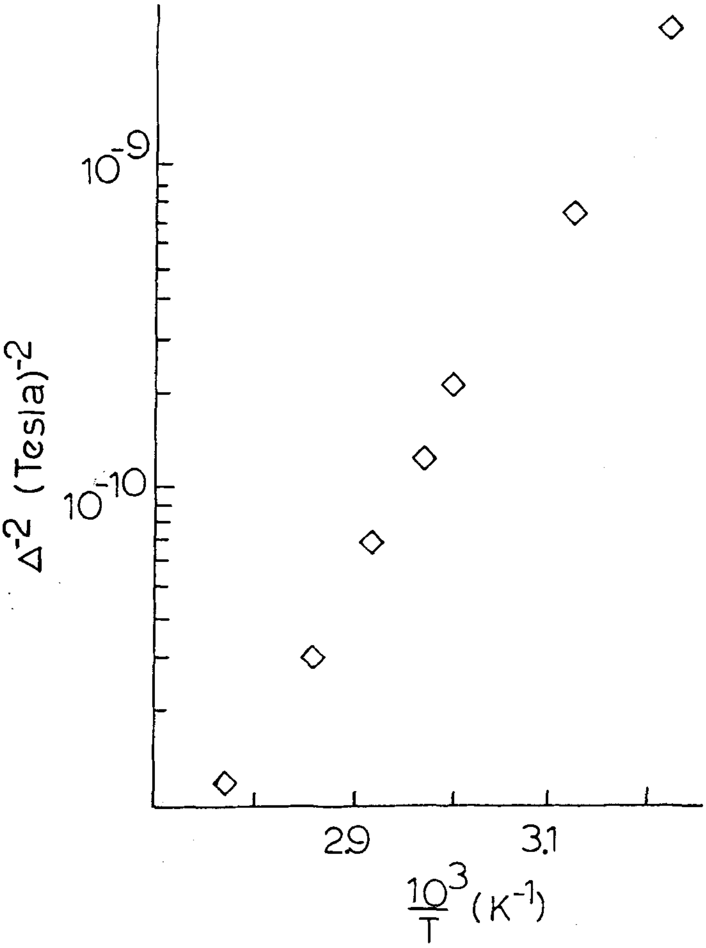

FIGURE 3 Plot of the log of the square of the reciprocal of the shift, Δ, of the low field extrema in hexamethyl benzene versus the reciprocal of the absolute temperature.

(c) Cyclohexane

Cyclohexane, C_6H_{12}, is an example of a solid which undergoes a solid-solid phase transition below the melting point in which there is an increase in the rotational degrees of freedom of the molecular subunit. In this case the molecule undergoes full rotation. These phases referred to as rotor or librator phases have transitional symmetry but no rotational order. Cyclohexane undergoes such a transition at 186 K from a monoclinic phase having C_{2h} (2/*m*) symmetry to a cubic phase where the center of mass of the molecules form a face centered cubic structure with the molecules rotating freely.[12] At 280 K this phase becomes liquid. The dynamics associated with the phase transition have been studied by a number of techniques such as NMR and Raman spectroscopy.[13,14] When liquid cyclohexane in which CuB is dissolved is cooled below 186 K a powder EPR spectrum is obtained. Figure 4 shows a plot of the inward shift of the low field extrema of this powder spectrum as a function of temperature as the material is warmed to the rotor phase. The inward shift Δ begins at about 186 K where the solid to rotor phase transition begins. A plot of the log $1/\Delta^2$ versus 1/K yields a straight line indicating that the correlation time of the rotation obeys Arrhenius kinetics. The average barrier to rotation obtained from five measurements is 0.48 ± .10 eV. which is in reasonable agreement with the barrier obtained from the temperature dependence of the NMR spin-lattice relaxation time which was 0.47 ± .04 eV.[13] Thus in the case of HMB and cyclohexane the observed motional effects in the EPR data correspond well to temperature regions in which other spectroscopies indicate evidence for motion.

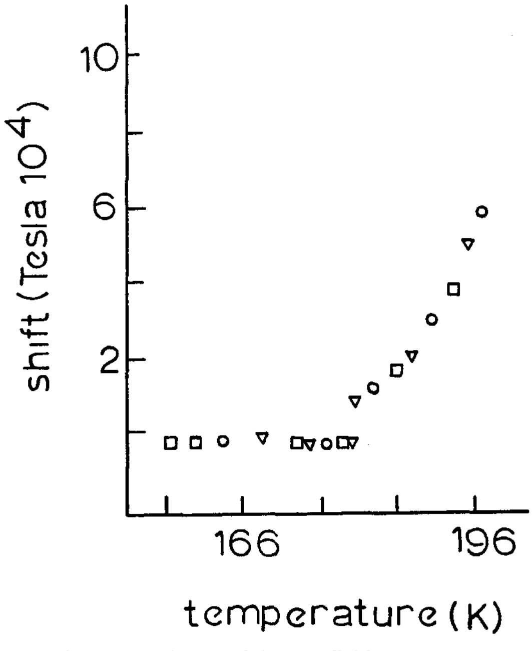

FIGURE 4 Plot of the inward shift of the low field extrema of the powder spectrum of CuB versus temperature through the 186 K librator transition in cyclohexane.

(d) P-methoxy cinnamic acid

Research in phase transitions in liquid crystals has mostly emphasized the liquid to liquid crystal transition and in fact EPR has been used as a tool to study the temperature dependence of the ordering process in the liquid crystal phase. However the dynamical processes in the crystal near the transition to the liquid crystal phase have not been the subject of much research. Some preliminary studies of the nematic liquid crystal para-azoxy anisole (PAA) have suggested the possibility of molecular motion in the solid prior to the transition to the liquid crystal phase. Marked reductions in neutron diffraction intensities, increases in diffuse scattering and reductions of the intensity of Raman lines have been observed in the crystal as the transition temperature is approached.[15,16] It has been possible to dope solid *p*-methoxy cinnamic acid with CuB. P-methoxy cinnamic acid (PMCA),

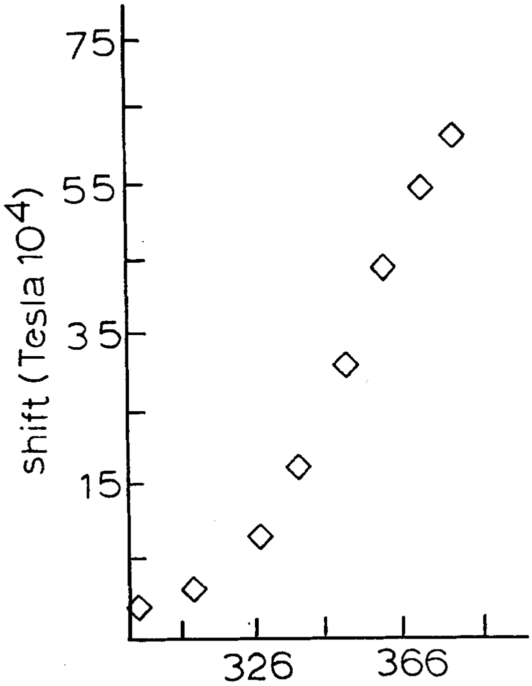

FIGURE 5 The temperature dependence of the inward shift of the low field extrema of CuB in the solid phase of the liquid crystal *p*-methoxy cinnamic acid as the solid to liquid crystal transition temperature is approached.

($CH_3OC_6H_4CH$:CHCOOH) undergoes a solid to nematic liquid crystal transition at 447 K. The nematic liquid crystal phase becomes isotropic at 465 K. As the temperature of the doped PMCA crystal is increased from room temperature to the solid to liquid crystal phase transition, T_{cn}, a marked inward shift of the extrema lines and a line broadening is observed. This is plotted in Figure 5. Figure 6 is a plot of the inverse square of the inward shift versus the reciprocal of the absolute temperature showing the correlation time of the motion of the probe obeys Arrhenius kinetics. A barrier to motion of 0.74 eV. is obtained. The data clearly indicate the CuB complex is undergoing slow tumbling in the lattice well below the melting temperature. A similar observation has been made in the liquid crystal *p*-methoxy-

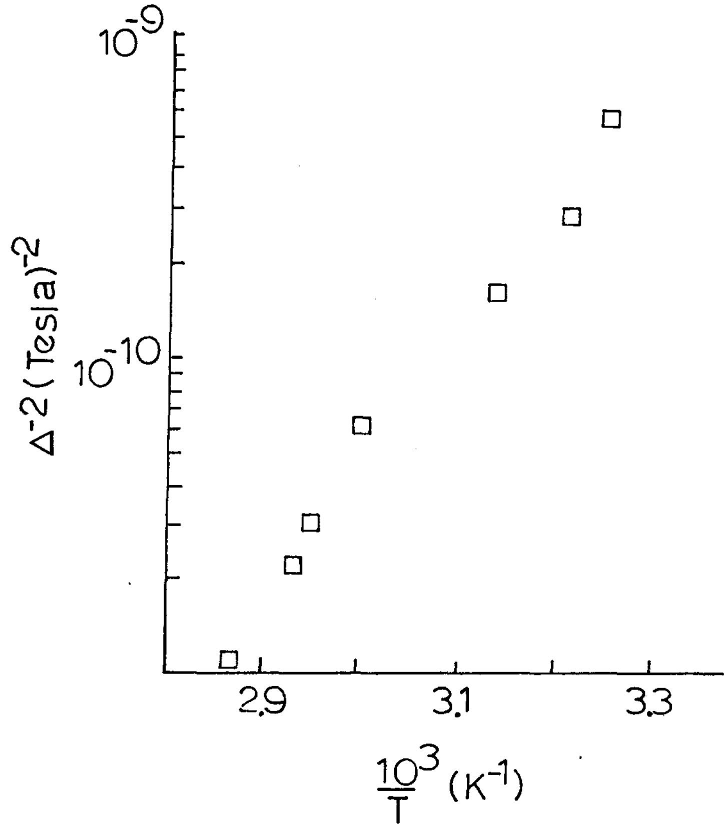

FIGURE 6 Plot of the log of the inverse square of the shift, Δ, of the low field extrema of the copper complex in the solid liquid crystal versus the reciprocal of the absolute temperature.

benzlidene amino phenyl acetate.[17] In the examples of HMB and cyclohexane discussed above the paramagnetic probe displayed motional averaging effects in the same temperature region in which other data indicated that the intrinsic molecules of the lattice motionally disordered. This suggests that the probe motion is driven by the intrinsic molecular motion. Thus the motion of CuB in PMCA suggests that the intrinsic liquid crystal molecules are undergoing thermally activated order-disorder motion in the crystal lattice prior to the transition to the liquid crystal phase. There appears to be then a high degree of motional disorder in the lattice prior to the transition. Further work is necessary in order to shed more light on the nature of the dynamics.

(e) Potassium and Ammonium Dihydrogen Phosphate

Potassium dihydrogen phosphate (KDP) is a well known hydrogen bonded ferroelectric undergoing a ferroelectric to paraelectric transition at 123 K. A high temperature phase transition has also been reported at 456 K about which little is known.[18] A reasonable possibility is that this high temperature transition is of an order-disorder nature involving fluctuations of the molecular anions analogous to such materials as KSCN[19] or RbN_3.[20] Further support for this possibility comes from high resolution single crystal neutron diffraction data in the paraelectric phase which were interpreted in terms of the $H_2PO_4^-$ molecule moving between two or more equilibrium positions.[21] A recent review of Raman scattering data in KDP has also led to the proposal of order-disorder behavior of the phosphate groups in the paraelectric phase.[22,23] In order to determine if there is such behavior at higher temperature in the lattice, the temperature dependence of the EPR spectrum of VO^{2+} doped into crystalline KDP was investigated. Good quality single crystals were obtained but the EPR spectrum of the VO^{2+} in them was complex and thus studies were made in finely ground powders in order to facilitate interpretation. Figure 7 shows that the low field extrema of the VO^{2+} powder spectrum does show an inward shift as a function of temperature beginning at 456 K close to the temperature of the reported high temperature phase transition. This evidence of motion at high temperature suggests that there is a high temperature order-disorder phase transition in KDP. The probe motion is governed by thermally activated Arrhenius kinetics. A similar shift is also observed in ammonium dihydrogen phosphate (ADP) at much lower temperatures suggesting also that there is an order-disorder transition in this material. The temperature dependence of the shift is shown in Figure 7. The barrier to motion in ADP was obtained to be 0.69 eV. and in KDP a value of 2.8 eV was obtained. The onset of the line shift in KDP corresponds to temperatures at which other measurements such as NMR show evidence for motion in Lattice.[24]

CONCLUSION

It has been shown that the onset of the order-disorder motion of the molecular subunits of a lattice can manifest itself as a motional averaging and therefore reduction of the anisotropic hyperfine splitting of a transition metal complex doped into the lattice. In the case of cyclohexane and HMB the beginning of the averaging corresponded to the temperature in which the molecular units of the lattice are known from other studies to undergo fluctuation. The kinetics obtained from the EPR data was in qualitative agreement with other measurements. In the case of cyclohexane the barrier to rotation of

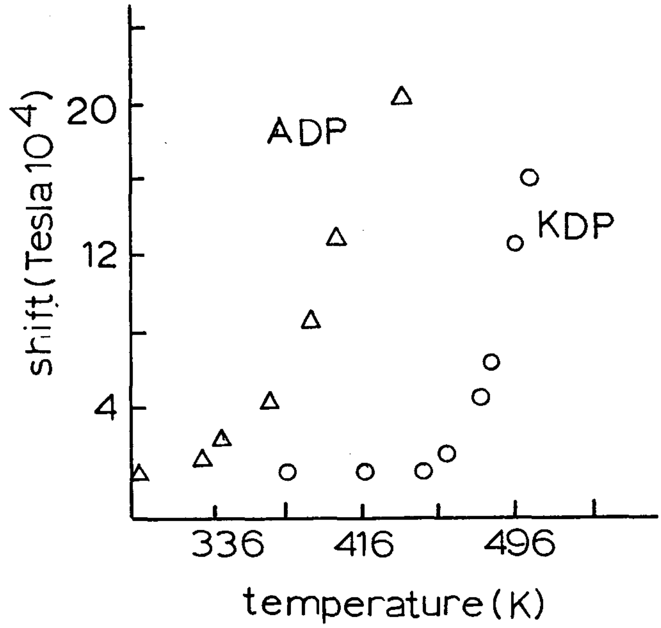

FIGURE 7 Plot of the inward shift of the low field extrema of the powder spectrum of VO^{2+} in potassium dihydrogen phosphate and ammonium dihydrogen phosphate as a function of temperature.

the probe was the same as that of the molecules of the lattice, however, in general there is no reason that this should be so. These results indicate that motional averaging of hyperfine splitting of dopant transition complexes can give information about dynamical processes occuring in structural phase transitions in particular order-disorder transitions. In the case of KDP where a phase transition has been reported at 450 K and where there is some evidence for motion of the anions, the EPR of VO^{2+} showed evidence for motion at 446 K, suggesting that this phase transition is of an order-disorder nature. Evidence was also found for the existence of a high temperature phase transition in ADP not previously known. Similarly the technique of motional averaging of hyperfine splitting has been used to provide evidence for the first time of molecular fluctuations of molecules in the solid liquid crystal PMCA. In the cases of KDP, ADP, and PMCA further work is necessary using other spectroscopic techniques to determine the nature of the phase transitions and the details of the dynamics. Even though the presence of the probe in the lattice produces considerable distortion of the local environment of the probe, the fact that the temperature of onset of motion of the probes corresponds to the temperature at which other measurements such as Raman and NMR show evidence for fluctuation suggests that the probe is sensing intrinsic bulk behavior.

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