

Phase transition studies of paramagnetic crystals at low temperatures

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Abstract. Magnetic, thermal, electrical and optical properties of a series of paramagnetic compounds of general formula $ABF_6 \cdot 6H_2O/6D_2O$ and $A(ClO_4)_2 \cdot 6H_2O$ where $A = Co, Na, Zn, Hg$ and $B = Si, Ti, Zr$, showing structural transition from room temperature hexagonal with one molecule in the unit cell to low temperature monoclinic with two molecules in the unit cell, are reviewed.

Keywords. Phase transition; paramagnetic crystals; low temperatures.

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1. Introduction

The beginning of the phase transition study of paramagnetic crystals was in 1956 when a number of experiments were performed at the Indian Association for the Cultivation of Science on the magnetic susceptibility of a series of double sulphate and double selenate chromic alums. The anomalous magnetic susceptibility behaviour observed in these alums in the temperature region 180 to 220 K was confirmed by Mitra *et al* (1964). However, the most important experiment in phase transition study of paramagnetic crystals was by Datta and Mazumdar (1965) who observed from magnetic anisotropy measurements in the temperature region 90–300 K, that the magnetic symmetry in $CoSiF_6 \cdot 6H_2O$ single crystals undergoes a transition at $T_c \sim 246$ K from uniaxial to orthorhombic. Dutta Roy and Ghosh (1968) obtained similar results in $CoF_2 \cdot 5HF \cdot 6H_2O$ and $CoZrF_6 \cdot 6H_2O$. It was also shown that the magnetic anisotropy anomaly observed in fluosilicates, hydrofluorides, and fluozirconates were due to a structural transition from room temperature hexagonal to low temperature monoclinic structure (Dutta Roy *et al* 1971). Chowdhury and Ghosh (1974) included a number of perchlorates in the series of paramagnetic crystals showing phase transition. Further evidences were given by Ghosh *et al* (1979), in deuterated fluosilicate and fluotitanate crystals. It is well known that a series of paramagnetic crystals of general formula $ABF_6 \cdot 6H_2O/6D_2O$ and $A(ClO_4)_2 \cdot 6H_2O/6D_2O$ where $A = Co, Mn, Fe, Zn, Mg$, and $B = Si, Ti, Zr$ undergo phase transition in the temperature region 77–300 K. Recently thermal (Sinha *et al* 1976), optical (Choudhury *et al* 1983), and electrical properties (Ghosh *et al* 1979) of these compounds have also revealed anomalous characteristics, at their respective transition temperatures. It is, therefore, important to review at this stage all the important results observed in these compounds for a possible

understanding of the interaction mechanism responsible for structural transition in paramagnetic crystals.

Section 2 describes the typical magnetic anisotropy results in fluosilicates including the pressure and dilution effect on the transition temperature. Heat capacity and thermal expansion results are given in § 3. Section 4 deals with electrical properties, the optical studies are presented in § 5 and the concluding remarks in § 6.

2. Magnetic anisotropy in $\text{ABF}_6 \cdot 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ and $\text{A}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ compounds

Extensive magnetic anisotropy data of the above compounds are available. Therefore, the magnetic anisotropic characteristics of a typical compound is shown in figure 1 where the magnetic anisotropy of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ in the symmetry plane as well as perpendicular to the symmetry plane is shown. It may be noted that the temperature variation of magnetic anisotropy in the plane containing the room temperature symmetry axis (*c*-axis) $\Delta\chi \cdot T^2$ shows an inflexion point near $T_c \sim 246 \pm 1$ K. The

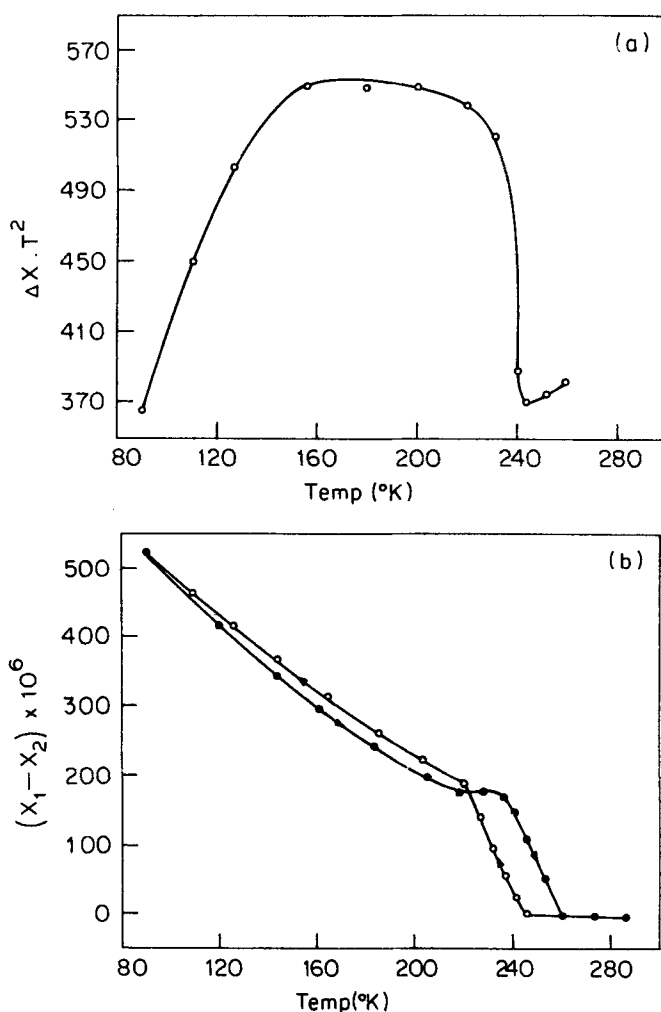


Figure 1. Magnetic anisotropy of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ in (a) the plane containing the *c*-axis; (b) the symmetry plane.

magnetic anisotropy in the plane perpendicular to the symmetry axis shows negligible anisotropy at room temperature. The anisotropy occurs at $T_c(c) \sim 246 \pm 1$ K and again disappears at $T_c(h) \sim 258 \pm 1$ K.

The effect of uniaxial pressure on the phase transition temperature is shown in figure 2 for $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$. The curves shown in figure 2(a) record the change occurring during the cooling process and have been plotted as $\Delta\chi \cdot T^2$ against T . The sharp inflexion points at 246 ± 1 K, 254 ± 1 K, 259 ± 1 K and 261 ± 1 K correspond to changes in transition temperature with pressure. Figure 2(b) indicates that $T_c(c)$ moves towards high temperature with increase of pressure.

The variation of transition temperature $T_c(c)$ with concentration x for $\text{Co}_{1-x}\text{Zn}_x\text{F}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$ and $\text{Co}_{1-x}\text{Zn}_x\text{SiF}_6 \cdot 6\text{H}_2\text{O}$ is shown in figure 3. The two

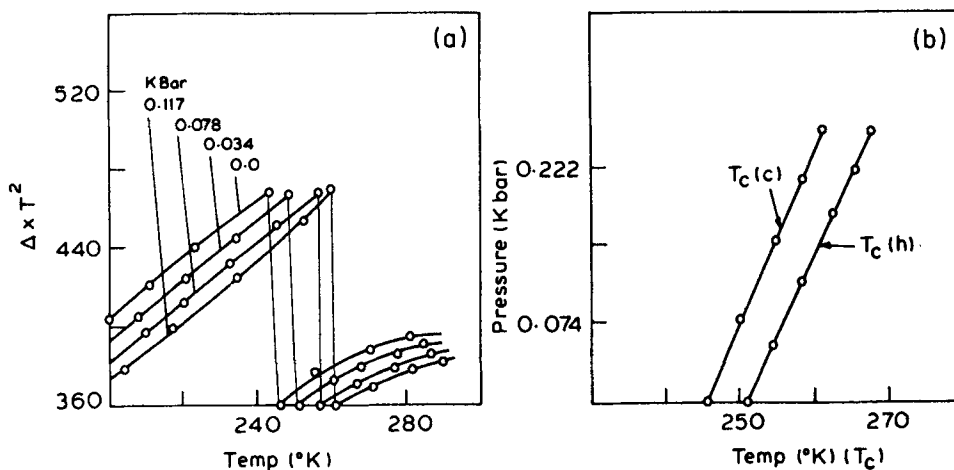


Figure 2. Effect of uniaxial pressure on the phase transition temperature, (a) change occurring during cooling process, (b) change of $T_c(c)$ as a function of uniaxial pressure.

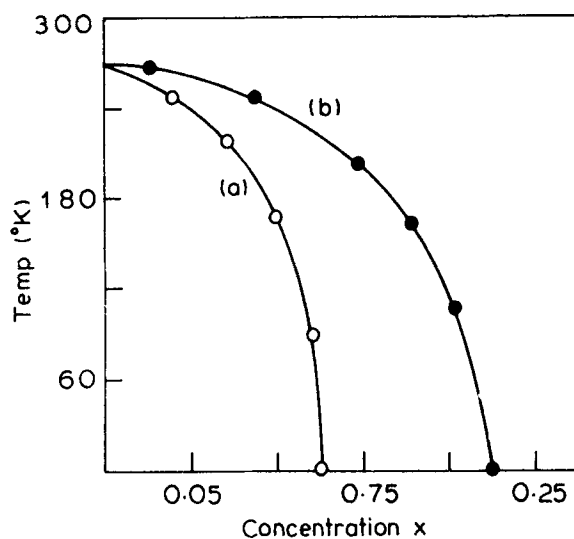


Figure 3. Variation of transition temperature $T_c(c)$ as a function of concentration x for $\text{Co}_{1-x}\text{Zn}_x\text{F}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$ and $\text{Co}_{1-x}\text{Zn}_x\text{SiF}_6 \cdot 6\text{H}_2\text{O}$.

curves indicate that $T_c(c)$ follows a nonlinear variation with concentration x . Also a critical concentration x_c exists at which the phase transition disappears. It is noteworthy that dilute crystals behave more or less in a fashion similar to those of the concentrated crystals except for the shift of the transition temperature towards the low temperature side as the zinc concentration in the crystal increases.

Low temperature structural data (Roy *et al* 1973) given in figure 4 show that in the unit cell of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, there are two types of Co^{2+} ions and the crystal symmetry is monoclinic with monoclinic axis (b_2) perpendicular to the room temperature hexagonal axis (C -axis). The ionic trigonal axes of the two Co^{2+} ions in the unit cell are oriented at angle ϕ with respect to room temperature hexagonal axis. The two types of Co^{2+} spins in the unit cell are at an angle ϕ_s with respect to room temperature hexagonal axis. Hence it is evident that the two sub-lattices are formed from adjacent Co^{2+} spins located in the two sites (A and B) whose ionic axes are tilted at an angle 2ϕ with respect to each other. Using the most general form of bilinear spin-spin coupling between two spins S_1 and S_2 in the two sublattices, Dutta Roy *et al* (1971) worked out the relationship between ϕ and ϕ_s using the method of Silvera *et al* (1964) and the final expression for the equilibrium angle of spins as,

$$\tan 2\phi_s = -\frac{2g_{\xi'} g_{\zeta'}}{g_{\xi'}^2 + g_{\zeta'}^2} \tan 2\phi. \quad (1)$$

If for $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ 2ϕ is calculated from low temperatures magnetic anisotropy data using the relationship for $K_{\parallel} > K_{\perp}$

$$\cos 2\phi = \frac{\chi_1 - \chi_3}{2(\chi_1 - \chi_2) - (\chi_1 - \chi_3)}, \quad (2)$$

where $K_3 = K_{\parallel}$ and $K_1 = K_2 = K_{\perp}$, is found out to be 24.6° . With this value of 2ϕ and anisotropic g values from the ESR observation of Bleaney and Ingram (1957) which are,

$$g_{\eta'} = g_{\xi'} = 2.796,$$

$$g_{\zeta'} = 4.235.$$

The angle $2\phi_s$ is calculated in equation (1) as,

$$2\phi_s = -22.8$$

which gives a spin-centering angle $\sim 0.9^\circ$ with respect to room temperature hexagonal

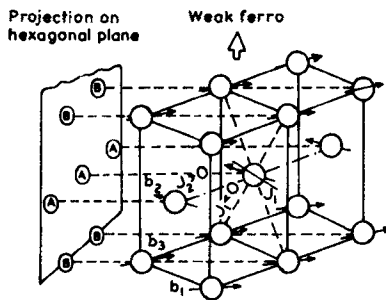


Figure 4. Low temperature crystal structure of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$.

axis. The result is in close agreement with low temperature magnetization data of Ohtsubo (1965). It is also to be noted that dilution experiment gives the information that after a critical value of dilution of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ crystal with $\text{ZrSiF}_6 \cdot 6\text{H}_2\text{O}$, the phase transition disappears, i.e., $\phi = 0$ and weak ferromagnetism also does not exist in dilute crystals.

3. Heat capacity in $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{A}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ compounds

The temperature variation of heat capacity of the three compounds in the series $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ is shown in figure 5, and the heat capacity of the three compounds in the series $\text{AB}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is shown in figure 6. Heat capacity anomaly observed in these compounds coincides with the transition temperature $T_c(h)$ obtained from magnetic anisotropy data. The characteristics of the transition in $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ compounds is that in region $T < T_c$ the heat capacity rises sharply with temperature whereas in the region $T > T_c$ the heat capacity decreases at a comparatively slower rate. In $\text{A}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ compounds, in the region $T < T_c$ the heat capacity increases at a comparatively slower rate and in the region $T > T_c$ the heat capacity falls sharply with temperature. An analysis of the heat capacity results around the phase transition

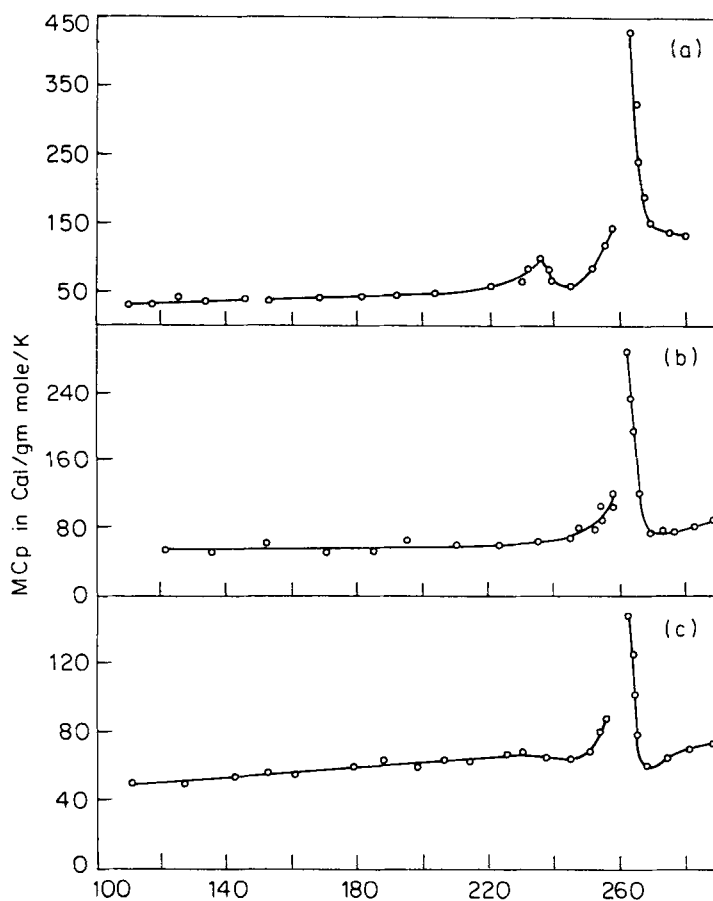


Figure 5. Thermal variation of heat capacity of the three compounds in the series $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$.

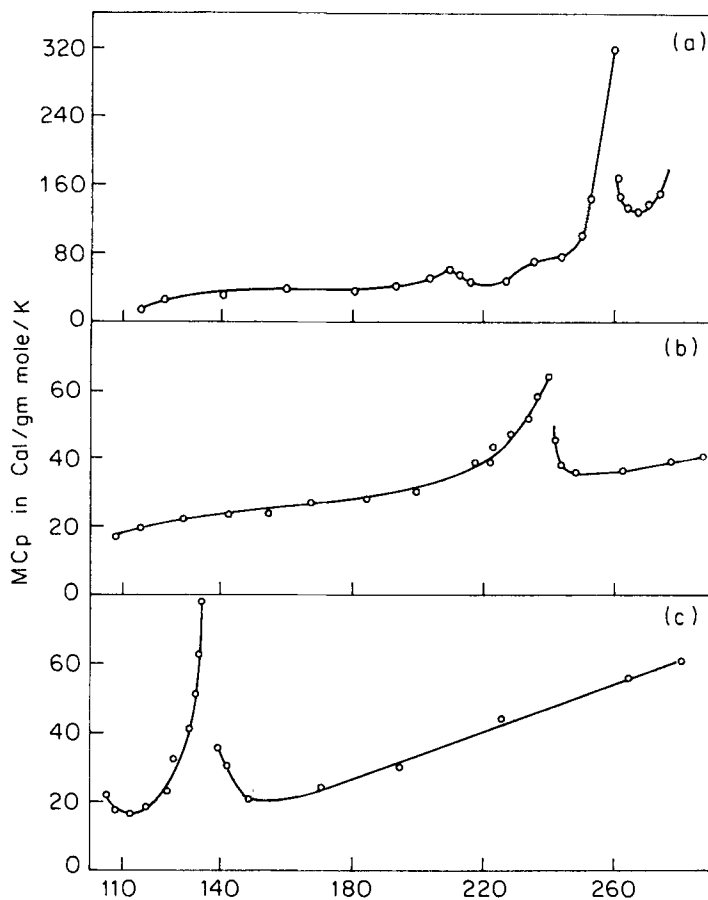


Figure 6. Thermal variation of heat capacity of the three compounds in the series $A(\text{ClO}_4)_2, 6\text{H}_2\text{O}$.

temperature suggests that a logarithmic singularity in the heat capacity exists both in $\text{ABF}_6, 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ and $\text{A}(\text{ClO}_4)_2, 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ types of compounds.

The temperature dependence of thermal expansion of one of the $\text{ABF}_6, 6\text{H}_2\text{O}$ compounds is shown in figure 7. From the anomalous temperature dependence of thermal expansion, information on the transition energy with pressure is calculated from the Clausius-Clapeyron equation

$$\frac{dT_c}{dp} = T_c \left(\frac{\Delta V}{L_0} \right), \quad (3)$$

where T_c denotes the transition temperature, L_0 , the latent heat and ΔV the volume change from the heat capacity data; heat of transition is 600 cal mol^{-1} or 4.257 cal/cc . The value of volume change ΔV is calculated from the thermal expansion data $\Delta l/l$ at $T_c(h)$. The value of dT_c/dp turns out to be -12.2 kbar^{-1} which suggests that the structural transition may have the first order origin.

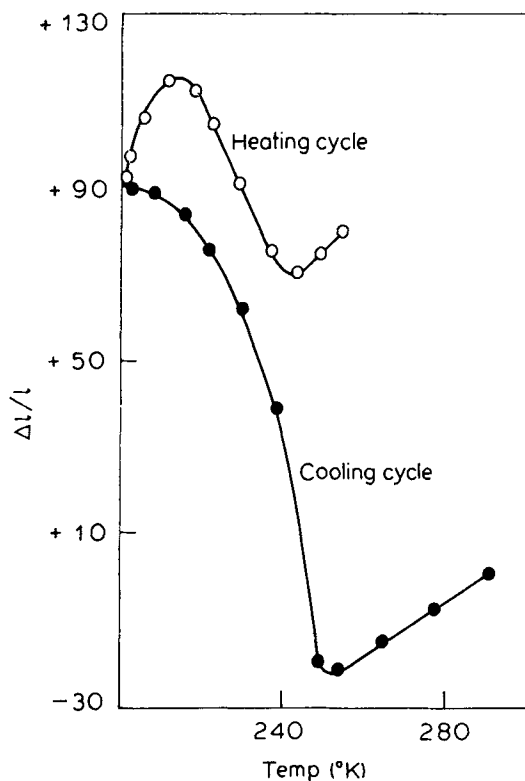


Figure 7. Temperature variation of thermal expansion of one of the compounds in the series $ABF_6 \cdot 6H_2O$.

4. Electrical conductivity of $ADF_6 \cdot 6H_2O$ and $A(ClO_4)_2 \cdot 6H_2O$

Figure 8 is a plot of electrical conductivity $\log \sigma$ as a function of T^{-1} for $CoSiF_6 \cdot 6H_2O$ and shows that conductivity decreases linearly with decrease in temperature down to 246 K maintaining a constant slope. At 246 K anomalous conductivity fluctuation of σ_{res} and σ_{true} occurs. The increase in conductivity is very sharp and $\log \sigma$ increases from π to $\bar{5}$ within a temperature spread of 2 K. During heating cycle $\log \sigma$ increases from π to $\bar{6}$. Figure 8 shows a similar conductivity plot for an ammonium chloride crystal for comparison.

The striking feature in the electrical property during transition is that in successive runs the conductivity jump in $CoSiF_6 \cdot 6H_2O$ crystal occurs at the same temperature $T_c \sim 246$ K, but the magnitude of the conductivity jump decreases appreciably in the second and the third run. As the crystal passes through the transition, a large number of internal cracks appear and this number increases in the successive run, resulting in lowering the magnitude of the conductivity jump in the transition region. Also an unusual feature in fluosilicate crystals is a disorder in the position in one of the six fluorine atoms between two sites unrelated by symmetry elements with unequal occupancy number (Roy *et al* 1973). It is presumed that the high electrical conductivity of $CoSiF_6 \cdot 6H_2O$ crystals at room temperature arises from the disordering of the ions in

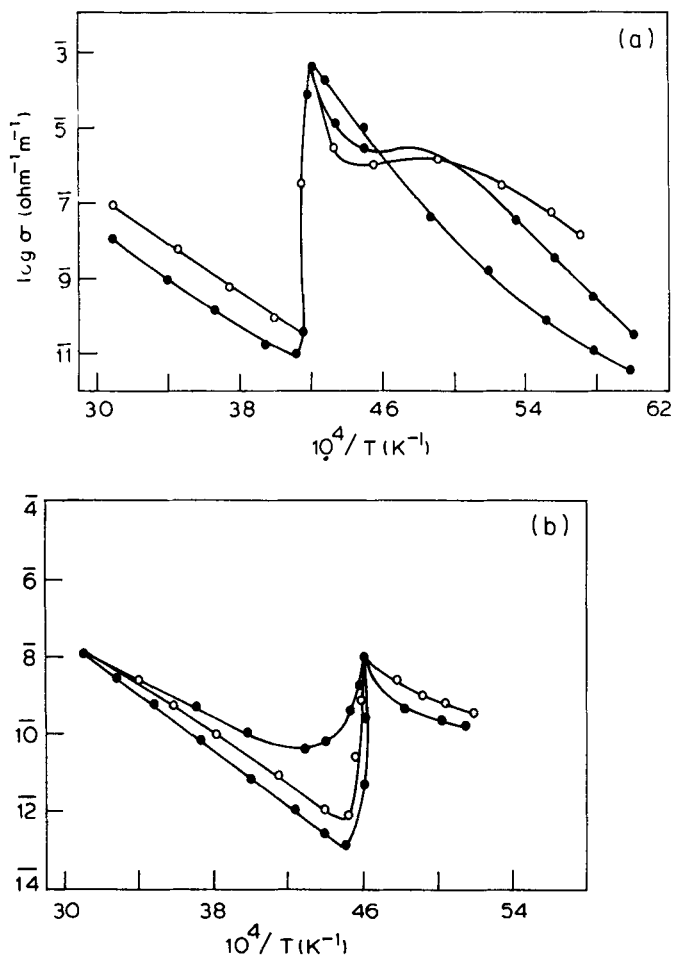


Figure 8. Electrical conductivity $\log \sigma$ as a function of T^{-1} for (a) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, (b) $(\text{NH}_4)_2\text{SO}_4$.

the lattice. In the transition zone disordering effect increases appreciably causing increase in electrical conductivity until the new crystal structure stabilizes.

5. Optical studies and mode coupling phenomena using Raman scattering

Choudhury *et al* (1983) studied the variation of Laser Raman spectra with temperature in $\text{ABF}_6 \cdot 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ system for various polarizations. A sharp change in the Raman intensity of the band 614 cm^{-1} has been observed in the YZ polarization at $200 \pm 3 \text{ K}$ during the cooling cycle and at $228 \pm 3 \text{ K}$ during the heating cycle. A feature common in all the observations (Chowdhury *et al* 1985) is that as one traverses from room temperature to a low temperature phase, the frequencies of vibration which are connected to $\text{A}(\text{H}_2\text{O})_6/(\text{D}_2\text{O})_6$ octahedra increase whereas those related to BF_6 octahedra decrease. This change in frequency depends on the strength of the coupling between the soft mode and the other modes.

6. Conclusion

The present results show that the study of temperature dependence of magnetic anisotropy in a series of compounds of the type $\text{ABF}_6 \cdot 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ and $\text{A}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is important in the understanding of structural transition phenomena in paramagnetic crystals. The crystals of the above compounds have shown a structural transition at T_c from hexagonal to monoclinic leading to anomalous changes in magnetic, thermal, electrical and optical properties. It is presumed that the interaction mechanism responsible for such a structural transition is to be obtained from a quantitative estimation of the frequency dependence of the strength of coupling between soft mode and other modes of vibration in the crystal.

References

- Bleaney B and Ingram D J E 1957 *Proc. R. Soc. (London)* **A208** 153
Chowdhury B K and Ghosh D 1974 *Phys. Status Solidi* **23** 651
Choudhury P, Ghosh B, Lambo O P and Bist H D 1983 *J. Phys.* **C16** 1609
Datta S K and Mazumdar M 1965 *J. Chem. Phys.* **42** 418
Dutta Roy S K 1956 *Indian J. Phys.* **30** 169
Dutta Roy S K and Ghosh B 1968 *J. Phys. Chem. Solids* **29** 1511
Dutta Roy S K, Ghosh B and Kar S 1971 *J. Phys. Chem. Solids* **32** 857
Ghosh B, Chatterjee N, Das A N and Chatterjee A 1979 *J. Phys.* **C12** 3283
Mitra S and Dutta Roy S K 1964 *Physica* **30** 1557
Mitra S S, Ghorai S K and Dutta Roy S K 1979 *Bull. Mater. Sci.* **2** 79
Ohtsubo A 1965 *J. Phys. Soc. Jpn.* **20** 82
Roy S, Zakin A and Templeton D H 1973 *Acta Cryst.* **B29** 2741
Silvera I F, Thornley J H M and Tinkham M 1964 *Phys. Rev.* **A136** 695
Sinha M P, Pal A and Dutta Roy S K 1976 *J. Phys.* **C9** 2783