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CRYSTAL LATTICE DYNAMICS AND PHASE TRANSITIONS MECHANISM IN POTASSIUM HYDRO (DEUTRIUM) SULPHATE CRYSTALS

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The phase transition in $KHSO_4$ crystals of varying deutrium content and different Cu^{2+} concentration is studied. The specific heat at constant pressure, C_p, and DTA measurements are investigated. The measurements are carried out in the vicinity of phase transition $T_c = 468$ K. Multiple peaks are observed in the temperature dependence of C_p and a noticeable change due to Cu^{2+} dopant. This behaviour can be attributed to the fact of order disappearance in partial melting of proton in sublattice.

Among solid electrolytes, it is usual to distinguish superionic conductors, which above certain temperature T_s have anomalously high ionic conductivity. One of the most thoroughly investigated families of superionic conductor [1-4] is the group of materials represented by the general formula: (M = Na, K, Rb, Cs atom or N_2H_5 and NH_4 group; BX_4 = SO_4'', SeO_4'' or BeF_4'').

Potassium hydrogen sulphates, $KHSO_4$, posses orthorhombic symmetry with space group D_{2h}^{15} and 16 molecules per unit cell [5, 6]. The unit cell dimensions are $a = 8.9$, $b = 9.19$ and $c = 18.93^{o}$A. Sunandana [7] detected the existence of two types of sulphate ions using electron spin resonance technique. In type I forming HSO_4-dimers, which are joined through two hydrogen bonds, type II forming a polymeric chain along the a axis by means

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of ladder type hydrogen bond. The microscopic theory of phase transition in protonic conductors was described as correlation between short range proton and hydrogen bond [8]. It was observed that KHSO4 crystals showed a structural phase transition at 468 K [9]. It is of interest to elucidate the influence of both deuteration and dopant on the phase transition temperature. These can be carried out by the measurements of electrical and thermal properties of pure, doped crystals with Cu^{2+} and deuterated KHSO4 crystal in the vicinity of the phase transition of such crystals.

Experimental techniques and measurements

Single crystals of KHSO4 were grown by isothermal and dynamical slow evaporation method from aqueous solution containing the initial salt. Deutrating of the crystal was done by recrystallization of KHSO4 three times

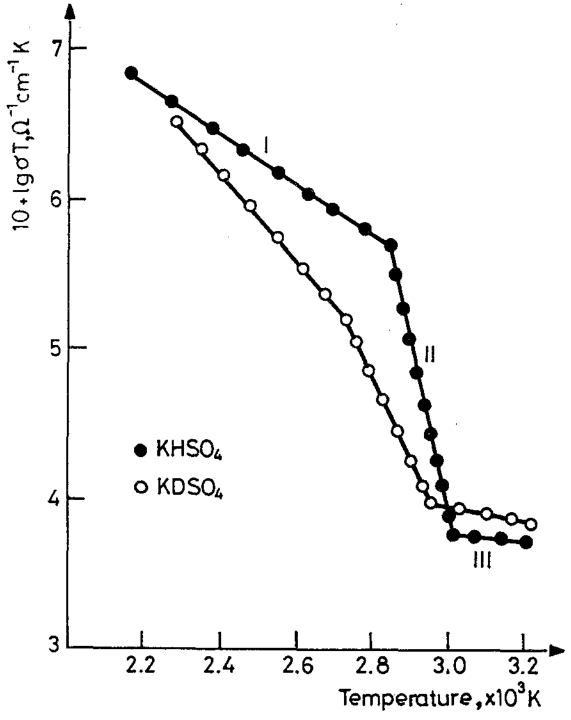

Fig. 1 Temperature dependence of electrical conductivity KHSO4 and KDSO4 crystals

in D_2O. Doping of the crystal with Cu^{2+} was done by adding specific amounts of $CuSO_4$ in the solution.

Electrical measurements were made using compressed samples of 1-2 mm thickness and 12.7 mm diameter.

Total conductivity was measured with a Wayne Kerr universal bridge type B 224 at frequency of 1592 Hz. Graphite electrodes (made from compressed powder) were used as contacts to the material. The details of the measurements are as published previously [11]. All measurements were done in vacuum using special holder [12]. The thermal measurements were carried out using Perkin-Elmer DSC-7 to measure specific heat in the temperature range 300-500 K. The detail of measurements are described elsewhere [13].

Results and discussions

1-Electrical conductivity:

Results of the log σT against the inverse of temperature are as shown in Fig. (1) for potassium hydrogen sulphate and potassium deutro sulphate samples.

In order to confirm the role of proton motion in the mechanism of the phase transition we have decided to investigate the influence of isotopic exchange on the phase transition. Figure (1) shows the the temperature dependence of electrical conductivity represented as log σT for fused samples of potassium hydrogen sulphate and potassium deutro sulphate. It is clear from Fig. (1) that a deuteration leads to a considerable shift of phase transition towards higher temperature [14]. This behaviour can be attributed to interaction between the potassium and tetrahedra which in effect, leads to disturbance of hydrogen bonds and decrease in significance of proton motion and to decrease the dipole moment per unit cell.

Figure (2) shows the temperature dependence of electrical conductivity for pure and Cu^{2+} doped $KHSO_4$. It is observed form Fig. (2) that the conductivity has an abrupt change in whole region of temperature of interest. The activation energies of the three linear regions are given by

	ΔE_I (ev)	ΔE_{II} (ev)	ΔE_{III} (ev)
$KHSO_4$	0.39	1.72	0.36
$KHSO_4 + Cu^{2+}$	0.32	0.48	0.06

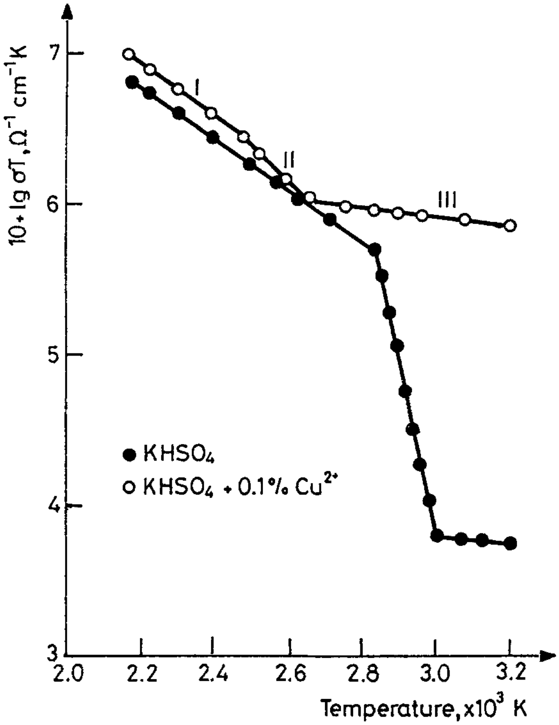

Fig. 2 Electrical conductivity log δT *vs.* $\frac{1}{T}$ for $KHSO_4$ together with $KHSO_4$ + $0.1^{\circ}10$ Cu^{2+}

The small variation in the activation energies of copper doped $KHSO_4$ sample is accompanied by a marked increase in the conductivity value which enable us to state that the effect is due to change in the carrier concentration rather than their mobility.

Thermal properties

The differential scanning calorimetry (DSC) data for $KHSO_4$ and $KDSO_4$ sample is as shown in Fig. (3). It is clear from Figure (3) that $KHSO_4$ crystals show a λ-type anomaly in the temperature dependence of the specific heat at 468 K. As a result of deuteration double peaks are found between 438 and 491 K. The appearance of double peaks on the C_p curve may be explained as a result of changes of the hydrogen bond character and the role of the proton dynamics is manifested in the change of the phase transition temperature at substitution of H to D atom and in this case the isotopic effect value at high temperature: $T_c = T_{c.D}\text{-}T_{c.H} = 5$ degree and the relative isotopic shift of transition temperature = 0.01.

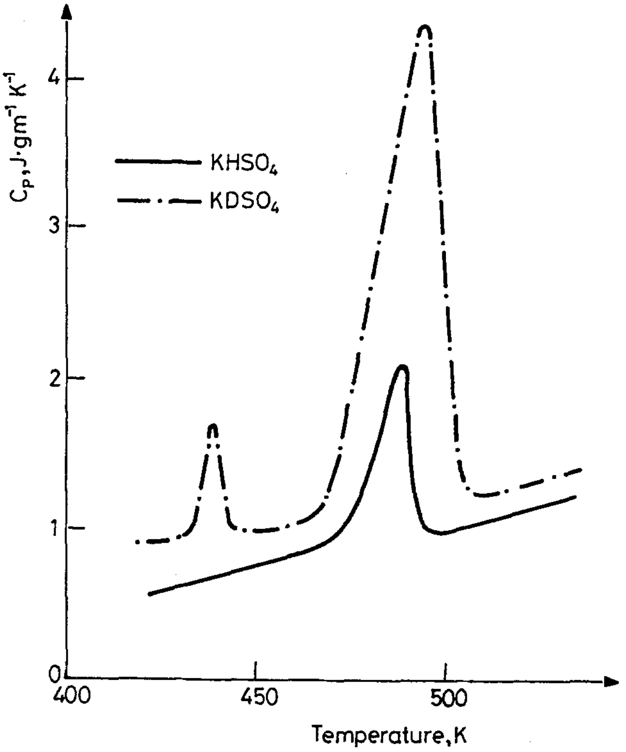

Fig. 3 Temperature dependence of specific heat at constant pressure, C_p, for pure and deuterated samples

The problem of defect and impurities upon the phase trainsition received our significant attention [13, 15]. The important goal of such study is to find out what properties of the crystals are really intrinsic and which ones connected with an inevitable defect.

Figure (4) shows the effect of Cu^{2+} dopand on C_p. It is clear from the figure that at Cu^{2+} content of 0.1 Cu^{2+} % the peak is shifted towords lower temperature and then a new peak appeared. As the Cu^{2+} content increases the peak is shifted again to higher temperature while the heat of transition is changed. It is clear also that the value of C_p changes sharply with Cu^{2+} concentration. The relatively strong increase in the specific heat of $KHSO_4$ containing admixtures of foreign ions suggests the possibility of the formal

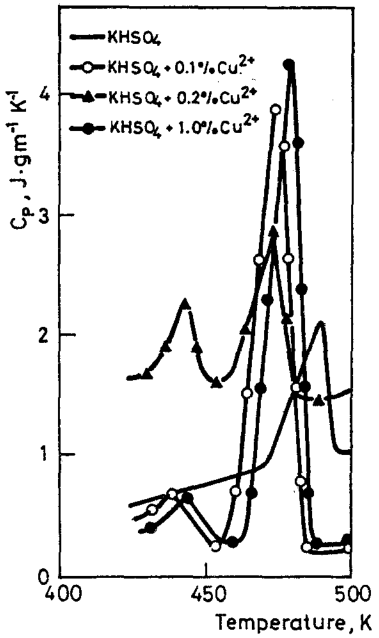

Fig. 4 Variation of specific heat at constant pressure, C_p, with temperature of pure and Cu^{2+} doped KHSO4 samples

approach of such crystals as two phase systems (at 1 % Cu^{2+} content) in which one phase consists of perfect crystal lattice KHSO4 and another of spherical or cubic regions of the lattice distorted by the presence of the foreign Cu^{2+} ions and consequently the specific heat is different in each phase.

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Zusammenfassung — Es wurde die Phasenumwandlung in $KHSO_4$ Kristallen mit unterschiedlichem Deuteriumgehalt und unterschiedlicher Cu^{2+}-Konzentration studiert. Die isobare spezifische Wärme C_p und DTA-Messungen wurden untersucht. Die Messungen wurden in der Nähe des Phasenumwandlungspunktes T_c = 468 K durchgeführt. In Temperaturabhängigkeit von C_p wurden Mehrfachpeaks sowie eine bemerkbare Änderung in Abhängigkeit vom Cu^{2+}-Gehalt beobachtet. Dieses Verhalten wurde erklärt.