

ELECTRICAL AND DIELECTRIC PROPERTIES OF NICKEL SULFATE HEXA- AND HEPTAHYDRATE SINGLE CRYSTALS

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ABSTRACT

Measurements of electrical conductivity (DC) and dielectric constant (10 kHz) in freshly prepared single crystals of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ have been carried out in the temperature range 30–450°C. It has been observed that the conductivity and dielectric constant show a large increase and decline at 100, 142, 186 and 360°C in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and 125, 210 and 365°C in the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals. The effect of melting is very well seen in the conductivity and dielectric measurements in the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals where a large but broad peak is observed between 45 and 115°C. The observed changes in conductivity and dielectric constant at the deaquation temperature have been explained on the basis of the release of water molecules at the respective deaquation temperatures and the subsequent dissociation of a fraction of these released water molecules into H^+ and OH^- ions. Availability of these charged particles increases the conductivity whereas the formation of space charge increases the dielectric constant.

INTRODUCTION

The sequence of deaquation steps in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ has been reported by several workers [1–6]. Fruchart and Michel [3] give the sequence of deaquation steps in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ as 1 mole, 2 moles, 3 moles and 1 mole while Sarig [4], from simultaneous TG, DTG and DTA measurements, suggested the deaquation steps as 1 mole, 3 moles, 2 moles and 1 mole at 60, 110, 130 and 330°C, respectively. Ben-Dor and Margalith [1] report that the sequence of deaquation steps in many polyhydrated metal sulfates consists of two definite steps. First, all but one molecule of water are evolved at a relatively low temperature (beginning at 60°C) and then, after a significant rise in temperature, the last molecule is released.

Thermal and electrical measurements have proved to be convenient methods for studying deaquation steps in many metal salt hydrate systems [7–10]. TG, electrical conductivity, and dielectric constant measurements on $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ single crystals were carried out by us [11,12]. It was observed that the electrical conductivity and dielectric constant both change at the deaquation step. It is reported [13] that, above room temperature (30°C), $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ is always transformed into $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$. It is also observed that, even if the sample is kept in a closed vessel, it slowly loses one molecule of water of crystallization. TG analysis of the

hexa- and heptahydrates of nickel sulfate shows the deaquation steps as 1 mole, 2 moles, 2 moles and 1 mole and 1 mole, 3 moles, 2 moles and 1 mole, respectively [14]. The phenomenon of melting was clearly seen in the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ but not in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$. With this difference in mind, it was thought fit to investigate the dependance of conductivity and dielectric constant on temperature using freshly prepared crystals. The results of this study in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ are presented in this paper.

EXPERIMENTAL

Nature of the samples

Nickel sulfate hexahydrate and heptahydrate powders of purity greater than 99.9% were obtained from Sarabhai Chemicals and B.D.H. Chemicals, respectively. Crystals were grown from the aqueous solution of these sulfates by slow evaporation at 40°C and 12.5°C . Crystals grown at 12.5°C were always heptahydrate and those grown at 40°C were always hexahydrate irrespective of the starting materials. Hexahydrate crystals have a prismatic shape whereas heptahydrate crystals have a plate-like growth.

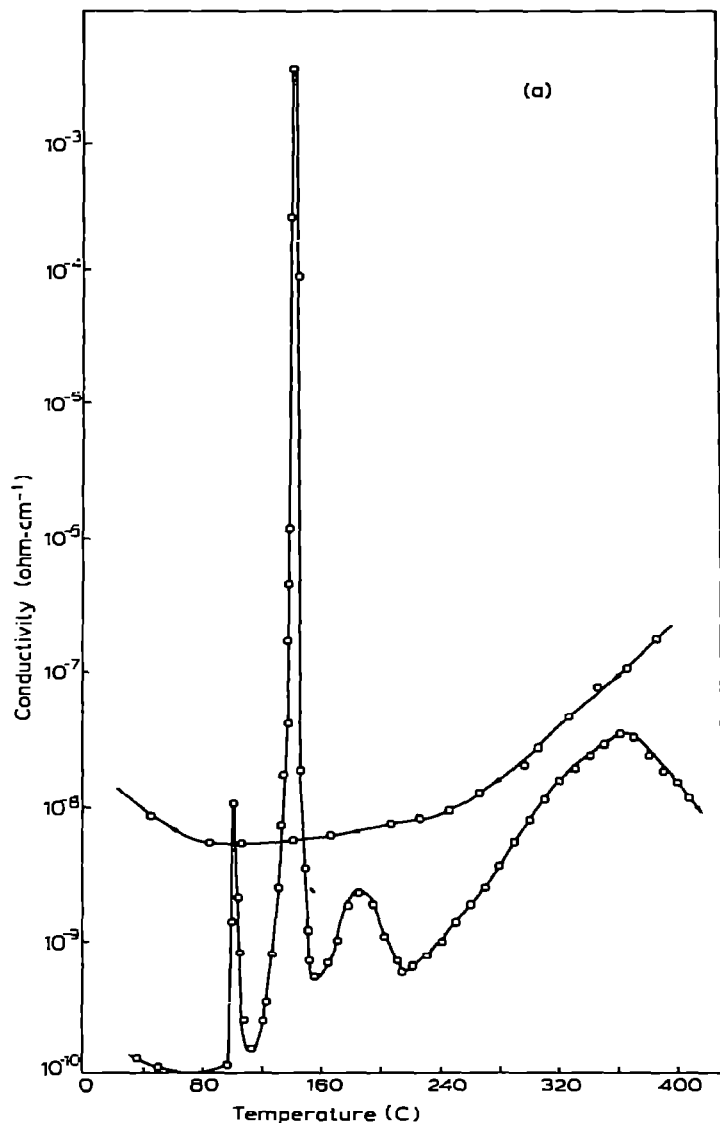
Measurements of electric conductivity and dielectric constant

The d.c. electrical conductivity was measured by the BPL meg-meg ohm meter type RM 160/3 in the temperature range $30\text{--}450^\circ\text{C}$. For measuring conductivity higher than 10^{-6} , a simple circuit was made which could measure it with the same accuracy as that of the meg-meg ohm meter. The heating rate was maintained at 1°C min^{-1} .

The dielectric constant was measured by a Marconi Universal Bridge type TF 868/1 at 10 kHz in the same temperature range. The heating rate was maintained at $0.5^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

The variation of $\log \sigma$ versus temperature for crystals grown at 40°C is shown in Fig. 1(a). It is seen from the figure that there are four sharp and distinct peaks at 100, 142, 186 and 360°C , respectively, in one of the sets. The height of the second peak is much larger and the last peak is much broader than the rest of the peaks. Figure 1(b) shows the plot of $\log \sigma$ versus T for crystals grown at 12.5°C . It is seen from the figure that the conductivity starts rising from 45°C , becomes very high (change of 7 orders of magnitude) and remains at this value up to about 115°C . Then the conductivity again rises giving a small peak at 125°C . Above this temperature, the conductivity immediately drops down to a much lower value. The conductivity again rises and falls at 210 and 365°C . On cooling, both the crystals show a continuous decrease in conductivity up to about 80°C after which it remains



more or less constant thereafter. The conductivity peaks observed on heating are completely missing on cooling.

Tanabe and co-workers [2] and Fruchart and Michel [3] give the deaquation steps in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ as 1 mole, 2 moles, 3 moles and 1 mole and Sarig [4] gives 1 mole, 3 moles, 2 moles and 1 mole at 60, 110, 130 and 330°C, respectively. Also, deaquation steps given by Berg and Kovyrina [5] and Demassieux and Fedroff [6], are as follows: 88°C, melting; 102--105°C, boiling; 166°C, dehydration; and 360°C, dehydration. We have studied [14] the difference in the deaquation steps of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals. $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ shows the same sequence of deaquation steps as given by Sarig [4], but the deaquation temperatures are entirely different. The observed temperatures from TG measurements are 130, 190, 210 and 380°C. $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ shows the deaquation steps as 1 mole, 2 moles, 2 moles and 1 mole at 129, 187, 214 and 390°C, respectively.

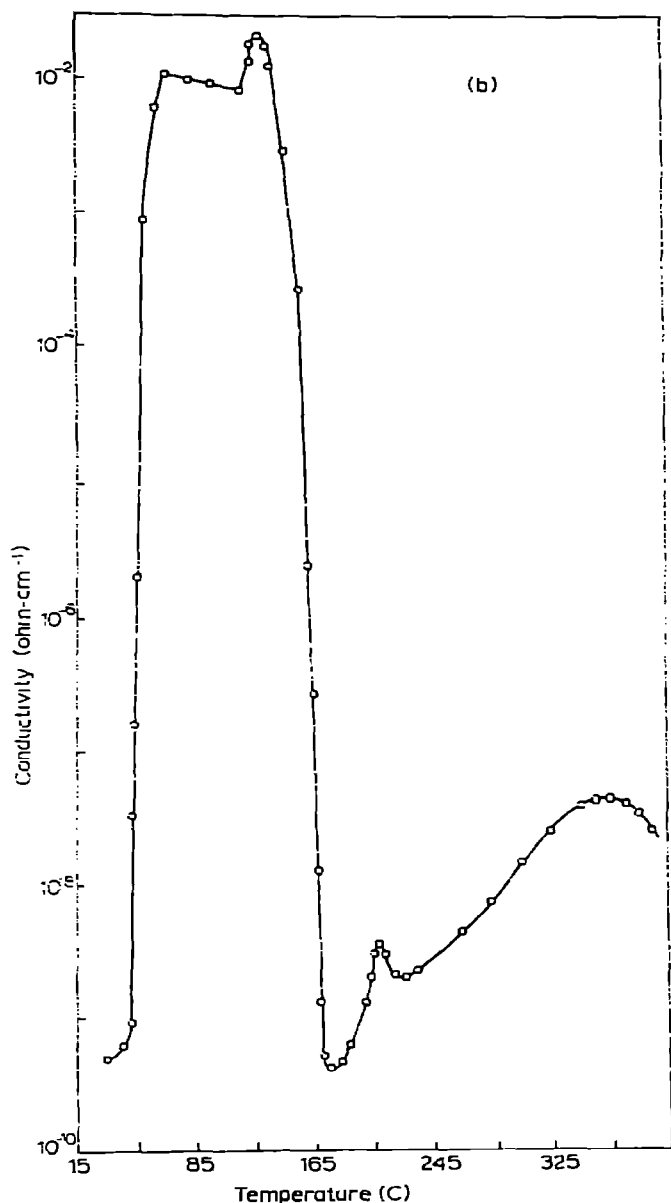


Fig. 1. Variation with temperature of the d.c. electrical conductivity of (a) a $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystal grown at 40°C and (b) a $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystal grown at 12°C .

The phenomenon of melting and subsequent boiling appear in the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals but not in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystals.

It is seen from Fig. 1(b) that the conductivity rises at 45°C to a very high value and remains high till a temperature of 115°C is reached. In the process of melting, 1 mole of water of crystallization is detached from the crystal structure and a part of it appears on the crystal surface dissolving some of the NiSO_4 material. In solution, Ni^{2+} and SO_4^{2-} ions are created. The ions are available for conduction and the conductivity increases to a very high value. The number of free ions decreases only on boiling the solution and therefore

the conductivity remains high up to this temperature. In this temperature interval, no loss of mass of the crystal was noticed. At the boiling temperature, the conductivity starts decreasing but then the deaquation starts and the crystal loses its water of crystallization in different steps at different temperatures. The conductivity peak due to deaquation is higher than that due to melting. This may be due to the fact that in melting the conduction is due to the Ni^{2+} and SO_4^{2-} ions and that in dissociation it is due to H^+ and OH^- ions and since the former ions are heavier than the latter, they have a lower mobility.

It is seen from Fig. 1(a) that the conductivity shows sharp rise and fall at 100, 142, 186 and 360°C which also correspond to different deaquation steps at those temperatures. In the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, there are only sharp peaks at the deaquation temperatures but at no temperature does the conductivity show a steady peak value as is observed in the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals. In $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals, the first broad conductivity peak is due to the availability of free ions in solution. But in the case of both crystals, the observed conductivity peaks at temperatures higher than the boiling temperature indicates that free charge carriers are available for conduction only during the deaquation process. It is therefore assumed that a very small fraction of the water molecules that are detached from the structure at different deaquation temperatures is dissociated into H^+ and OH^- ions. This increases the concentration of mobile charge carriers causing the observed large increase in conductivity at the dehydration temperature. It is observed that in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, the change in conductivity is maximum for the second deaquation step in which two molecules are involved. In the case of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$, the second conductivity peak, which corresponds to the deaquation of three molecules, has the greatest height. The heights of the conductivity peaks at other temperatures depend on the fraction of the water molecules dissociated into the respective ions.

The number of charged particles, n , collected during the peaks of the conductivity curves can be determined experimentally by calculating the area under the current vs. time curve corresponding to the total charge released near the respective deaquation temperatures and dividing this by e , the charge of the electron. Figure 2 gives the variation of current with time for $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystals. The number of charged particles obtained in this way is 2.79×10^{12} for the first step, 1.33×10^{17} for the second step, 1.71×10^{14} for the third step and 3.69×10^{15} for the last step in one of the experimental sets for $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$. The data for $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals is summarized in Table 1.

Using Maxwellian distribution and assuming the dissociation energy of H_2O to be 1.2 eV in water, the fraction, f , of water molecules dissociated after being detached at the respective deaquation temperatures can be calculated. Let

$$f = \frac{\text{the number of water molecules dissociated}}{\text{the total number of water molecules detached}} = \frac{n_2}{n_1}$$

where n_2 is the number of water molecules which receive thermal energy greater than $(kT + 1.2)$ eV and n_1 is the number of water molecules which

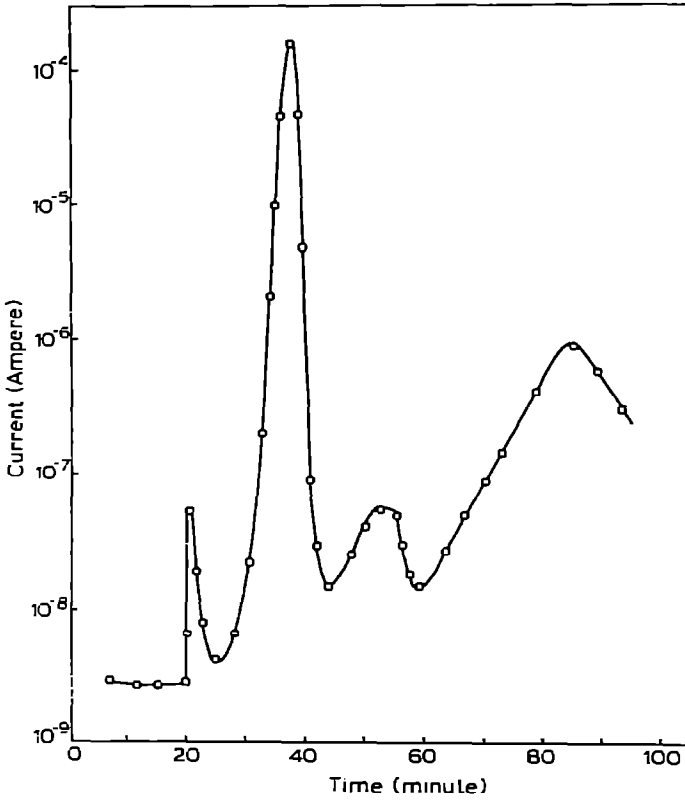


Fig. 2. Plot of current against time for calculation of the number of charge carriers produced by dissociation of a $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystal.

receive thermal energy greater than kT . From Maxwellian distribution

$$f = \frac{n_2}{n_1} = \frac{\int_{kT}^{\infty} e^{-E/kT} dE}{(kT + 1.2)}$$

Let f be the ratio of the number of water molecules dissociated, n_2 , to the total number of water molecules, N , that correspond to the first deaquation temperature.

$$f = \frac{n_2}{N}$$

where

$$N = \int_0^{\infty} e^{-E/kT} dE$$

The number of water molecules dissociated, n_2 , i.e. the number of free positive and negative charges produced at the deaquation temperature is equal to

TABLE 1

Values of the number of charged particles produced at each deaquation step and the corresponding values of dissociation energies for $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals

	Deaquation step		
	Second	Third	Fourth
Experimental values of n_2 (calculated from area)	9.36×10^{18}	1.97×10^{14}	4.85×10^{15}
Statistical values of n_2 assuming $E = 1.2 \text{ eV}$	5.41×10^5	1.69×10^8	9.39×10^{10}
Assumed values of the dissociation energies (eV)	0.15	0.62	0.60
Statistical values of n_2 assuming val- ues of E given in row 3	8.81×10^{18}	1.91×10^{14}	4.86×10^{15}

$f \times$ (total number of water molecules, N , corresponding to the first deaquation temperature). N is of the same order of magnitude as n_1 , i.e. $N \cong n_1$. Hence $f = f'$. Therefore the number of water molecules dissociated will be $N \times f$. N can be calculated by assuming that, in the case of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, out of the six water molecules 1 mole is involved in the first peak, 2 moles in the second, 2 moles in the third and 1 mole in the last peak. These calculations give the number of charged particles produced after dissociation for $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystals as 1.73×10^4 for the first deaquation step, 1.50×10^5 for the second, 2.88×10^6 for the third and 7.85×10^{10} for the fourth, which are lower than the experimentally observed values. This may be explained by assuming that the dissociation energy of H_2O in the crystal depends on the strength by which the H^+ and OH^- ions in the H_2O molecule are pulled in opposite directions in the crystal structure and therefore may be lower in solids than in liquids where the molecules are free. It is found that if the dissociation energy of H_2O in the crystal structure is chosen to be 0.594 eV for the first step, 0.298 eV for the second, 0.588 eV for the third and 0.610 eV for the fourth step, then the statistical calculations give the number of the charged particles due to dissociation as 2.64×10^{12} for the first step, 1.34×10^{17} for the second, 1.72×10^{14} for the third and 3.89×10^{15} for the fourth, which are in close agreement with the experimental values. As pointed out above, the decrease in dissociation energy of the H_2O molecule inside solid $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ may be due to the pulling of the OH^- ion by the Ni^{2+} ion in one direction and H^+ ions by the SO_4^{2-} ions in the opposite direction. Dissociation energies in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystals for H_2O molecules at different temperatures have been calculated in a similar manner and are also summarized in Table 1.

The bonding in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ has been discussed in detail by Evans [15] and the structural properties have been correlated with the thermal properties by Sarig [4]. $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ is just a modification of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ wherein the first water molecule has already been removed from the structure. The deaquation steps in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ are given as 1 mole, 3 moles, 2 moles and 1 mole. The removal of the first water molecule from $\text{NiSO}_4 \cdot 7$

H₂O during the crystal growth at 40°C converts it into NiSO₄ · 6 H₂O. The remaining water molecules are rearranged in such a way that the second deaquation step consists of 3 moles being split into two different steps of 1 mole and 2 moles, altering the bonding strength of these molecules and giving the deaquation steps as 1 mole, 2 moles, 2 moles and 1 mole.

At the respective deaquation temperatures, the different water molecules are released and a fraction of them is dissociated. All the water molecules so released and dissociated are not able to leave of the crystal immediately and many of them remain trapped in the interstitial space. The dissociated and the trapped H⁺ and OH⁻ ions are made mobile by the applied field contributing to the large increase in conductivity. As the temperature passes the deaquation point, the number of trapped ions decreases at a high rate as they are driven by the applied field and collected by the respective electrodes, thus giving the conductivity peaks. The water molecules released from the crystal structure but trapped in the interstices can come out relatively slowly by the diffusion process. Hence the deaquation steps given by thermogravimetry (which is only concerned with the loss of mass) occur at temperatures higher than those given by conductivity measurements. Table 2 summarizes the values of deaquation temperatures for both the crystals from different studies.

Figure 3 shows plots of dielectric constant versus temperature for NiSO₄ · 6 H₂O and NiSO₄ · 7 H₂O crystals. It is seen from the figure that the dielectric constant measurement also shows peaks at the respective deaquation temperatures given by the conductivity measurements on the crystals. The melting phenomenon in the case of NiSO₄ · 7 H₂O crystals gives rise to

TABLE 2

Deaquation temperatures from TG, conductivity and dielectric constant measurements

Step	From TG ^a		From conductivity			From dielectric			
	T_m [K(°C)]	Δm	S	T_m [K(°C)]	Δm	S	T_m [K(°C)]	Δm	S
NiSO₄ · 7 H₂O									
I	400 (130)	4.89	1.22	343 (70)	3.5	1.02	343 (70)	3.5	1.02
II	463 (190)	9.78	2.11	397.5 (124.5)	3.75	0.94	395 (122)	3.6	0.91
III	483 (210)	8.88	1.83	473 (200)	10	2.11	463 (190)	9.5	2.05
IV	653 (380)	6.66	1.02	633 (360)	5.04	0.79	631 (355)	7.1	1.1
NiSO₄ · 6 H₂O									
I	402 (129)	4.7	1.16	371.5 (98.5)	2.9	0.78	369.7 (96.7)	3.9	1.05
II	460 (187)	6.7	1.45	418.2 (145.2)	2.9	0.69	412.2 (139.2)	4.2	1.02
III	487 (214)	9.6	1.97	464.8 (191.8)	4.8	1.03	482 (209)	10.9	2.26
IV	663 (390)	9.7	1.46	630 (357)	2.1	0.33	650 (377)	5.6	0.86

^a T_m = mean temperature, Δm = mean deviation in T and % S = percentage spread in the temperature.

The data is from the earlier paper by the authors (ref. 14). The first deaquation step in NiSO₄ · 7 H₂O is judged from the centre of the broad peak in conductivity and dielectric constant measurements. T_m has been calculated from different sets of observations.

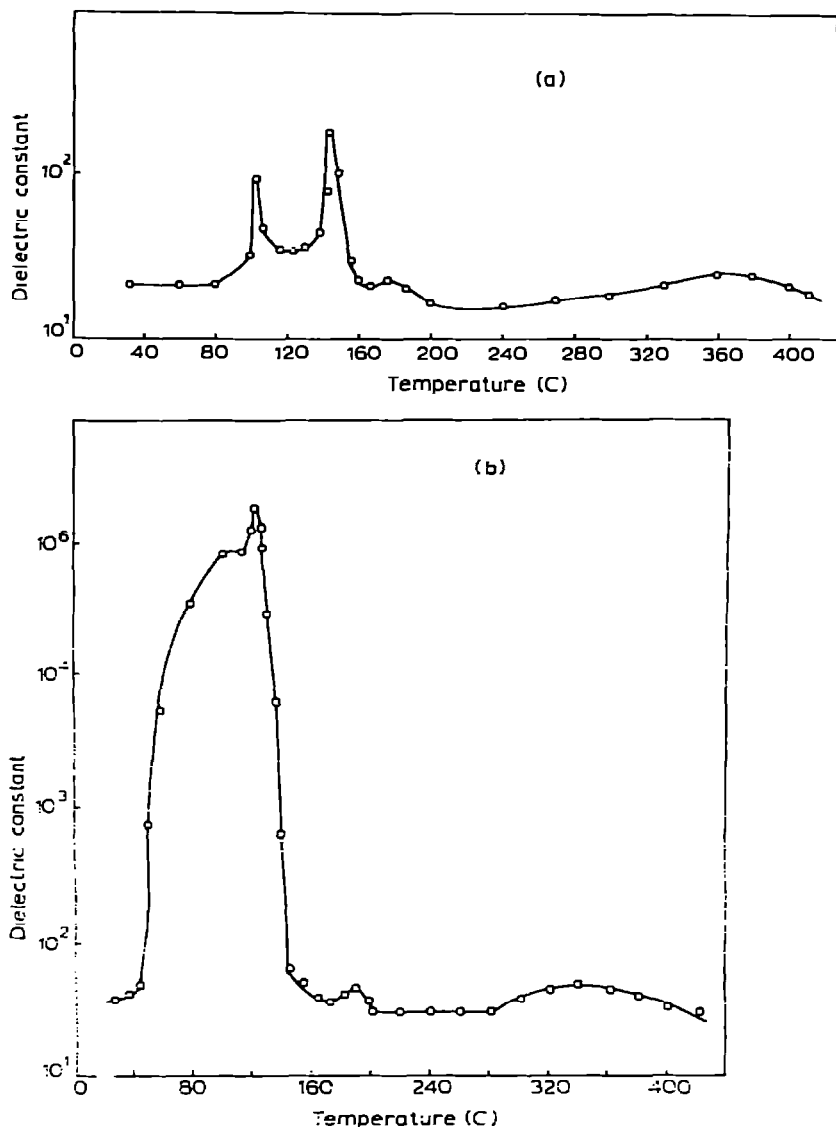


Fig. 3. Variation of the dielectric constant with temperature of (a) a $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and (b) a $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystal (frequency 10 kHz).

a very large change in dielectric constant (five orders of magnitude) and also increases the loss ($\tan \delta$). In many cases, the loss becomes so great that the dielectric constant measurement becomes unreliable. As soon as the liquid is boiled off, the loss decreases and so also does the dielectric constant. Beyond this temperature, both $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystals show peaks in the dielectric constant at the respective deaquation temperatures, indicating a connection between the deaquation steps and the dielectric constant. The increase in the dielectric constant is due to the orientation of the permanent dipoles of the water molecules released from the crystal structure but trapped within the material and to the space charge polarization produced by the trapped positive and negative charges generated after dissociation of the water molecules. On cooling, however, the dielectric constant is found to

remain constant from 430°C to room temperature. Absence of any such change in the dielectric constant and conductivity on cooling supports the assumption of dissociation of water molecules at the respective deaquation temperatures.

CONCLUSIONS

It is concluded from the study that the conductivity and dielectric constant show marked variations in crystals where the phenomenon of melting occurs. At the deaquation temperatures also there are sharp changes in conductivity as well as dielectric constant but the nature of these changes is quite different from those observed in the case of melting. Beyond the melting temperature, $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystals have almost identical behaviour. The deaquation temperatures given by the conductivity and dielectric studies are lower than those given by TG measurements.

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