PHYSICAL REVIEW B VOLUME 40, NUMBER 7 1 SEPTEMBER 1989

Ionic conductivity and the phase transitions in Na_2SO_4

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(Received 18 January 1989; revised manuscript received 22 March 1989)

The electrical conductivity of single crystals of Na_2SO_4 has been measured along the three principal crystallographic axes at temperatures in the range 160–400 °C. The measurements reveal a hitherto unsuspected large anisotropy in the Na^+ ion conduction in the stable room-temperature orthorhombic phase (V) of the as-grown crystals. The conductivity is restricted largely to the (010) crystallographic plane and is attributed to open tunnels in the [101] and [$10\bar{1}$] directions that form an interconnected network facilitating Na^+ ion diffusion. On heating, a pretransition region of sample-dependent conductivity occurs at 226 °C followed by a sluggish but major structural transition at 241 °C to a hexagonal phase (I). The microscopic details of this atypical irreversible transition are discussed. On cooling, further transitions to phase II (at 234 °C) and phase III (at 229 °C) occur, while on heating phase III transforms directly to phase I (at 249 °C). The conductivity in phase I, II, and III is nearly isotropic and the activation energies are essentially independent of crystal orientation in each phase.

I. INTRODUCTION

Sodium sulfate (Na_2SO_4) exhibits a number of structural phase transitions between several phases often referred to as I to V. These transitions have been widely studied[1–12] using differential thermal analysis (DTA), differential scanning calorimetry (DSC), specific heat, electrical conductivity, x-ray, and Raman scattering methods. The high-temperature phase (I) occurs below the melting point (884 °C) and the crystal transforms from $I \rightarrow II \rightarrow III$ on cooling. Phase II is an intermediate phase that exists within a narrow temperature range near 230 °C and phase III is metastable at room temperature. On reheating, transition $III \rightarrow I$ takes place without occurrence of an intermediate phase. The stable phase at room temperature is phase V, and on heating it transforms eventually to phase I at approximately 240 °C. There have been many controversial reports[1–11] on the existence and nature of an intermediate phase (thought by some authors to be phase III) between phase V and I.

The crystal structure of phase V is orthorhombic, space group $Fddd$ (D_{2h}^{24}),[13] and the high-temperature phase I is hexagonal, $P6_3/mmc\,(D_{6h}^{4})$.[14] The other room-temperature phase (III) also has orthorhombic symmetry, $Cmcm$ (D_{2h}^{17}),[15] but the structure of intermediate phase II is not yet known. The presence of another intermediate phase IV between phase V and I has yet to be firmly established and has been discarded in recent studies.[6,7,9] Here we note that there are two well-characterized room-temperature forms, V and III. Phase III was reported to be quite stable for more than one year at room temperature when the Na_2SO_4(III) sample was contained in dried air.[4,6] However, in the normal atmosphere phase III slowly reverts to phase V. The mechanism of this conversion in Na_2SO_4 is entirely unknown but it most likely involves water molecules.

Most of the previous thermal analysis studies of Na_2SO_4 were performed on powder or pressed pellet samples and it has been determined that the occurrence of polymorphism is dependent on the method of sample preparation,[3,6,10,11] i.e., particle size, pressure of die, grinding time, and water contamination. In the case of conductivity measurements, again most results have been reported from powder measurements,[7,12,16–19] although there has been one single-crystal study.[7] The single-crystal study was on an unoriented sample and involved one heating cycle only. The powder measurements have concentrated mainly on the high-temperature behavior (phase I) and there are considerable differences in the values obtained for the absolute conductivity and activation energy. We report here measurements of the electrical conductivity along all three crystallographic axes of oriented single crystals of Na_2SO_4.

Na_2SO_4(I) is known to exhibit a high ionic conductivity at high temperatures due to the increased mobility of Na^+ ions. It is now well known that high ionic conductivity values are related mainly to intrinsic structural features. Since the ionic conductivity values well reflect the structural changes,[20,21] it is expected that single-crystal conductivity measurements should provide more information about the structural phase transitions of Na_2SO_4 than the previously much-studied thermal analysis methods.

II. EXPERIMENTAL

Colorless crystals of Na_2SO_4(V) were grown from aqueous solution at 50 °C by slow evaporation of the solvent. Crystals of bipyramidal shape grew to a size of $\sim 20 \times 30 \times 35$ mm^3 with well-developed (110) and (111) faces. Sodium sulfate cleaves readily along (010) planes. We confirmed the crystallographic axis orientation by x-ray diffraction and we found that the unit-cell dimensions of our Na_2SO_4(V) sample were very similar to Nord's structural data.[13] We prepared from 5 to 10 samples of typical thickness 1.5 mm and area 15 mm^2 (with evaporated gold contacts) for each crystal axis study. For comparison, we also prepared compressed polycrystalline samples. The crystals were crushed finely and pelletized at 8 tons/cm^2. Prior to the evaporation of gold the pellets were annealed for more than 12 h at a temperature below 200 °C. The sample under investigation was mounted in a triply insulated alumina tube and a programmable temperature controller was used for automatic control of the successive heating and cooling cycles. Most of the measurements were performed with heating and cooling rates of 10 °C/h, but sometimes we used a very slow rate of 2 °C/h. The electrical conductivity was measured at 10 kHz using a HP 1492A impedance analyzer and recorded on an *xy* plotter. Prior to the adoption of this fixed frequency technique the complete response from 5 Hz to 13 MHz of selected oriented crystal and powder samples at a variety of temperatures was assessed by the use of complex plane analysis. Absolute conductivities were determined from considerations of the sample shape, but due to irregularities in the sample forms and imperfections within the samples we estimate that overall our absolute values could be in error by as much as 10%.

III. RESULTS

Figure 1 shows a typical impedance plot of a [001] oriented sample. At low frequencies the points lie on an inclined straight line and at high frequencies it shows the typical circular response. For the sample of Fig. 1, the minimum point, which gives the true resistance, is at ~1.4 kHz and the resistance value at 10 kHz is only 0.7% smaller than that at 1.4 kHz. For other specimens at a variety of temperatures in our usual measurement range of 160 to 320 °C, we found that the minimum points occur for frequencies between 1 and 50 kHz. Because of this sample-dependent variation in the minimum point frequency, we adopted the fixed frequency of 10 kHz for this study as it lies near the middle of this range. From our complex plane analysis of a selected group of samples we found that the resulting errors in the resistance measurement at 10 kHz were within the range −6% to +8%. Use of the continuous measurement technique at one frequency enabled us to follow rapid changes in the conductivity with temperature change near the phase transitions.

Figures 2 and 3 show the conductivity of Na_2SO_4 single crystals in the [100] and [001] directions. It can be seen that the overall features of the conductivity data in these two directions are similar. In the first heating cycle (process 1) the conductivity of phase V increases smoothly till $T_1 = 226\,^\circ C$. At T_1, a slight change of curvature is seen and then it increases until $T_2 = 241\,^\circ C$. At T_2, the conductivity decreases rapidly, indicating a major transition to phase I. In our measurements, most of the samples show a slight change of curvature at T_1 in their conductivity values, but sometimes a small peak appears at T_1. Here we note that the major transition at T_2 is very sluggish: The transition temperature range is sample dependent and extends from 7 to 10 °C with a heating rate of 10 °C/h.

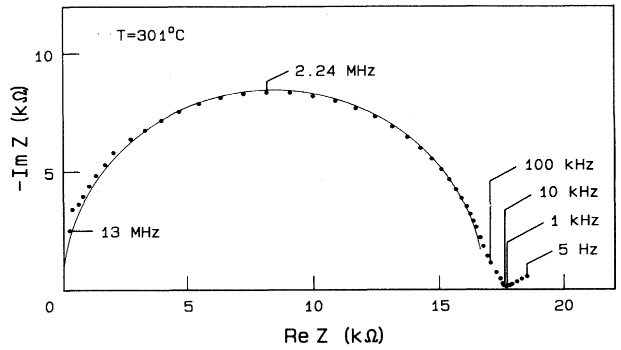

FIG. 1. Complex impedance spectrum of single-crystal Na_2SO_4 at 301 °C for the [001] direction.

In the first cooling (process 2), it can be seen that the transitions I→II→III take place, but the intermediate phase II appears very weakly as indicated by a slight change in the conductivity. In the second cooling (process 4), phase II appears more clearly and there is no further hysteresis on subsequent cooling cycles. Some samples were temperature cycled up to 400 °C, with no apparent effect on the phase II hysteresis phenomenon. The transition temperatures of I→II and II→III are 234 °C and 229 °C, respectively. The fact that the low-temperature phase in the cooling process is phase III rather than phase V is now well established from x-ray

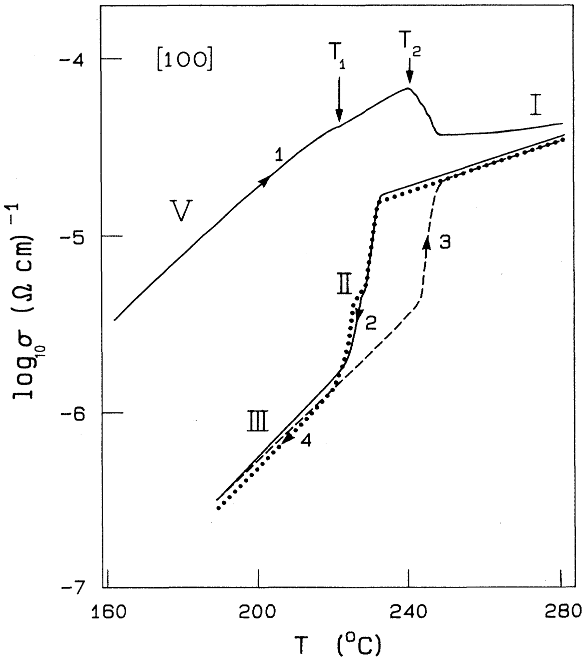

FIG. 2. Temperature dependence of the electrical conductivity of single-crystal Na_2SO_4 for the [100] direction.

and Raman measurements.[6,8–10] In the second heating (process 3), there is a III→I transition at 249 °C without any apparent occurrence of an intermediate phase and there is no hysteresis on subsequent heating cycles.

Figure 4 shows conductivity values along the [010] direction. The ionic conductivity along the *b* axis is very low in phase V and is approximately 10^{-8} $(\Omega\,\mathrm{cm})^{-1}$ at 200 °C (the sample resistance at temperatures below 220 °C was too high for accurate measurements with our impedance analyzer). This value is more than 1000 times smaller than that along the [100] and [001] directions. It shows clearly that the ionic transport process in Na_2SO_4(V) occurs mainly in (010) planes. In the next thermal cycles, the I→II→III transitions on cooling and the III→I transition on heating are also clearly visible in the [010] direction data. Thus, in contrast, the conductivity in phases I and III is nearly isotropic, as can be seen from Figs. 2–4.

Figure 5 shows representative results for the conductivity values of polycrystalline pellets. The phase transitions take place over rather broader temperature intervals than in single crystals. The first anomaly at $T_1 = 226$ °C is not well observed, but the other major transitions are well reproduced, as in the single crystal.

We have already mentioned the sluggishness of the nature of the V→I transition at T_2. To investigate more precisely the nature of the V→I transition we measured conductivities with a very slow heating rate, 2 °C/h, and the data is shown in Fig. 6. It shows that the transition temperature range at the T_2 transition is reduced to within 2 °C and the sluggishness has nearly disappeared. This suggests that the true nature of the V→I transition at T_2 is an abrupt one of the first-order type even though the stabilization time of the new phase is long. The changes in [100] and [001] conductivity observed at T_1 are much weaker than at the 10 °C/h heating rate (compare Figs. 3 and 6). The slower rate of 2 °C/h on cooling reproduced the 10 °C/h result.

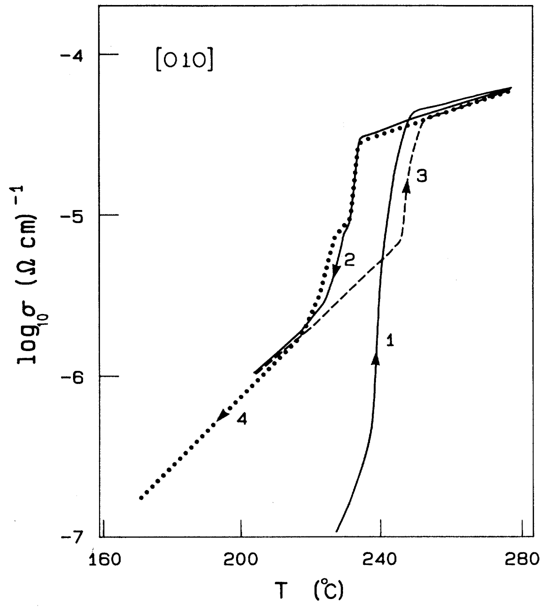

FIG. 4. Temperature dependence of the electrical conductivity of single-crystal Na_2SO_4 for the [010] direction.

The ionic conductivity of a solid is often described by an Arrhenius equation

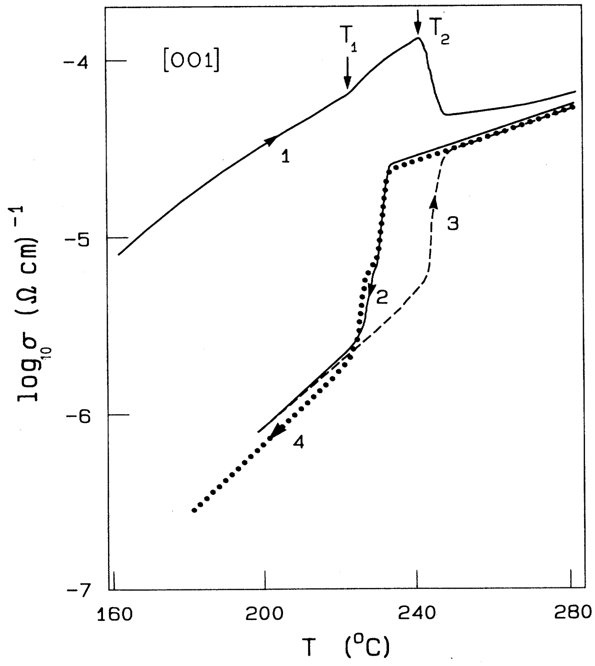

FIG. 3. Temperature dependence of the electrical conductivity of single-crystal Na_2SO_4 for the [001] direction.

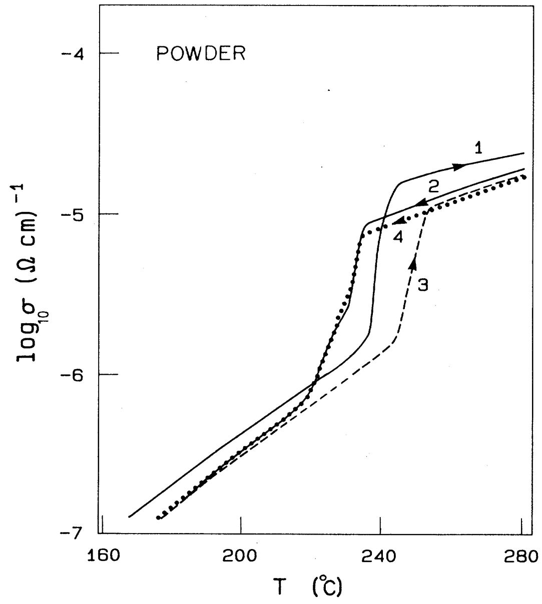

FIG. 5. Temperature dependence of the electrical conductivity of polycrystalline pellet Na_2SO_4.

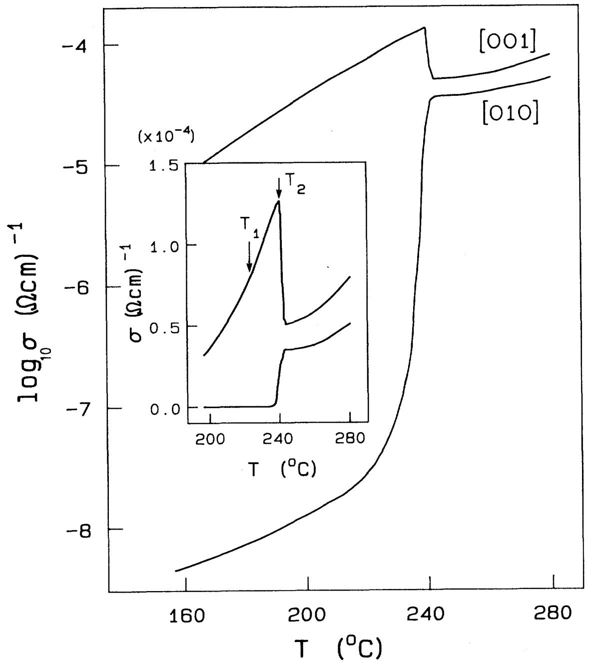

FIG. 6. Temperature dependence of the electrical conductivity of Na_2SO_4 single crystals for the [001] and [010] directions measured with a slow heating rate of 2 °C/h. The inset shows a linear conductivity scale for comparison.

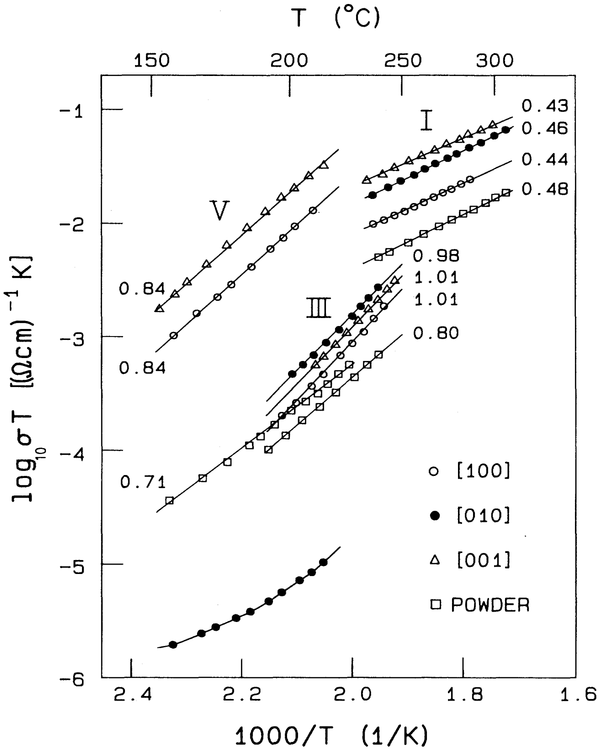

FIG. 7. Arrhenius plot of the ionic conductivity of Na_2SO_4. The numbers besides the lines are activation energies in eV and the Roman numbers indicate the phase. Data for phase V are taken from the first heating process, phase I from the first cooling, and phase III from the second heating.

$$\sigma = (C/k_B T)\exp(-E/k_B T) ,$$

where E is the activation energy, k_B is Boltzmann's constant, and C is a prefactor. For comparison, we have replotted the conductivity data in the form of $\log_{10}\sigma T$ versus $1/T$ as shown in Fig. 7. The conductivities of phases I, III, and V are well represented by straight lines for all crystallographic directions, except for the b-axis direction in phase V. This discrepancy may arise in part from errors in using single frequency data, but it is mostly due to the difficulty of accurately measuring the very low conductivity values at temperatures below 220 °C (see Fig. 6). Conductivities of phase I in polycrystalline samples have been reported in many papers,[7,12,16–19] but there is a considerable variation in the conductivity values obtained and the corresponding activation energy. Our results from polycrystalline samples agree with the data of several recent papers: The activation energy of 0.48 eV determined in phase I is close to the reported value of ~0.5 eV found in the extrinsic conductivity region of pure Na_2SO_4 samples.[18,19] In the single crystal, Fig. 7 demonstrates clearly that the phase V is quite anisotropic in its behavior, while phases I and III are nearly isotropic. It also shows that the activation energy is virtually independent of the crystal orientation in each phase (excluding the b axis in phase V).

We now comment on the mechanical stability of the crystal. The crystal was found to remain transparent although several tiny interior cracks were visible after several heating and cooling cycles in our measurement range (160–320 °C, 10 °C/h). Using a microscope we observed that these tiny cracks appear just at the T_2 transition, and at any other transitions no new cracks appeared although the original cracks became larger. When the crystal was brought down to room temperature, many cracks and milky regions appeared at temperatures below approximately 100 °C. Another observation worth noting is that in repeated heating-cooling cycles between phases III and I the conductivity measured at any given temperature was always lower than that obtained in the previous cycle, that is, a family of parallel $\log_{10}\sigma$ versus T curves was obtained. The steady decrease in absolute conductivity with each temperature cycle is most easily explained as being a consequence of the tiny cracks mentioned earlier growing slightly in size after each cycle through the sharp transition.

IV. DISCUSSION

Figure 8 shows the essential features of the room-temperature structure of $Na_2SO_4(V)$. The crystal lattice consists of two interpenetrating face-centered lattices. To develop some qualitative feeling for the nature of the Na_2SO_4 V→I transition, we note that the structure of phase V forms a relatively open $SO_4{}^{2-}$ framework. In the structure, there are two kinds of tetrahedra formed from sulfate molecules; one (consisting of points 2,3,5,6) contains another $SO_4{}^{2-}$ ion (point 7), but the other

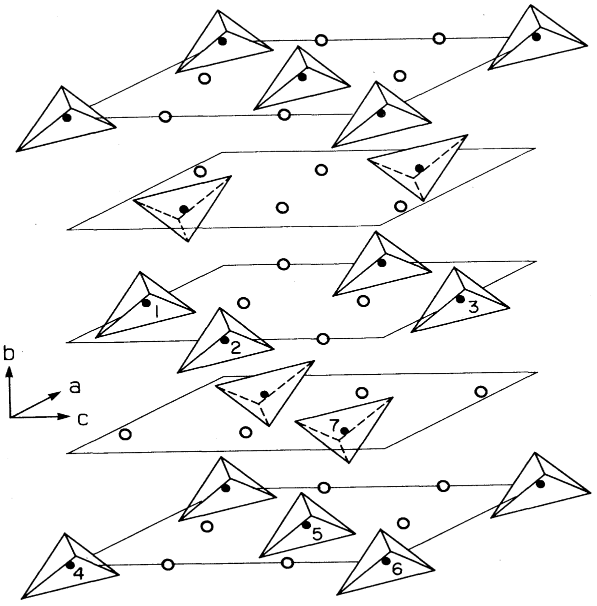

FIG. 8. The crystal structure of phase V of Na_2SO_4. The *b* axis is exaggerated for clarity. The open circles are Na^+ ions. The numbers denote $SO_4{}^{2-}$ ions. One tetrahedron consisting of numbers 2, 3, 5, and 6 contains another $SO_4{}^{2-}$ ion (number 7), but the other (numbers 1, 2, 4, and 5) is relatively vacant.

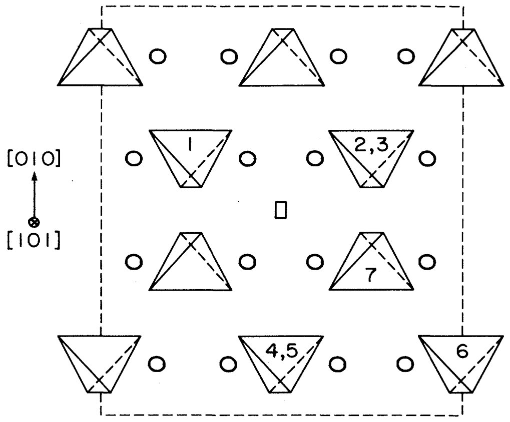

FIG. 9. The structure of phase V projected along the [101] direction. The open circles are Na^+ ions. The numbers are included for comparison with Fig. 8. The square denotes the center of an open tunnel.

(points 1,2,4,5) is relatively vacant (it contains two Na^+ ions spaced ~3.61 Å apart at room temperature). We consider these vacant sites where the $SO_4{}^{2-}$ ions are missing to play a key role in the ionic conduction in phase V and in the structural transition to I. As will be shown later, these vacant sites are connected to form an open network in (010) planes and thus give high conductivity values in this plane. Since the two kinds of tetrahedra are connected alternately in space and, thus, the density of $SO_4{}^{2-}$ lattice points is spatially so nonuniform, it may be expected that Na_2SO_4(V) will transform at an elevated temperature to a more uniform and, consequently, higher-symmetry phase.

The large conductivity anisotropy of phase V can be easily understood from the structure, as shown in Fig. 9. There are open tunnels in the [101] and [10$\bar{1}$] directions and these form an interconnected network in the (010) plane. This network provides a readily accessible diffusion path for the mobile Na^+ ions and allows high-conductivity values in the [100] and [001] directions. It is well known that one of the most important factors for fast ion conduction is the presence of an open, rigid structure formed by the immobile species. In Na_2SO_4(V), it seems that the open structure in the (010) planes plays such an important role in the diffusion of Na^+ ions that the conductivity along the [010] direction is lower by three orders of magnitude than in the other directions (see Figs. 6 and 7). We also note that the conductivity in the [001] direction of phase V is about two times larger than that in the [100] direction (see Figs. 2, 3, and 7). This difference might arise from the fact that the open tunnel in the [101] direction makes an angle of 30.8° with the [001] axis at room temperature. This angle gives a factor of 1.7 (tan30.8°) for the relative conductivities along the [100] and [001] directions. Thus, if we consider experimental errors in measuring the absolute values of conductivity, it is quite plausible that the directionality of the open tunnel is the main cause of the conductivity difference.

There are several inconsistencies in the published reports about the existence of an intermediate phase between V and I.[1–12] The intermediate phase has been regarded frequently as phase III and the reported values of the V→III and III→I transition temperatures are also diverse, varying by as much as ~40 °C. Sometimes it was reported that multiple transitions take place in between phases V and I according to the sample preparation.[1,3,10] However, from our conductivity data on the oriented single crystals we can discard the possibility of phase III as an intermediate phase between phases V and I, since (i) the conductivity change at T_1 is so smooth that it does not indicate any abrupt structural change (the crystal structure of phase III is orthorhombic and it is very different from orthorhombic phase V, but not that much different from hexagonal phase I),[14] (ii) the conductivity values in the [100] and [001] directions between T_1 and T_2 are very much different (more than 20 times larger) from those of phase III that occurred on the subsequent cooling and heating process (see Figs. 2 and 3), and (iii) the conductivities between T_1 and T_2 exhibit a large anisotropy, as in phase V, but the ionic conduction in phase III is nearly isotropic (see Figs. 2–4 and 7). From these comments and from the fact that the conductivity values between T_1 and T_2 deviate slightly from the extension line of phase V values, it can safely be assumed that the skeleton structure of this intermediate state is nearly the same as that of phase V. Kracek, in his earlier x-ray powder-diffraction study,[2] reported that at about 220 °C (~T_1) the diffraction pattern shows indications of a structural change taking place, and a new pattern indicating a structural phase transition has occurred is obtained at temperatures beyond 240 °C (~T_2). Kolontsova *et al.*[22] reported the same kind of x-ray observations in K_2SO_4 single crystals at temperatures above 400 °C, and those were regarded as indications of a pretransition region in advance of the structural transition at 580 °C. The pretransition is considered to be a preparatory stage caused by structural changes not associated directly with the formation of the new phase. Cazzanelli and Frech[23] also pointed out recently, from their Raman scattering studies on Li_2SO_4 single crystals, the possibility of the existence of a pretransitional region above 450 °C which seemed to be characterized by the onset of significant reorientational disorder of the sulfate ions. In this regard, we can conclude tentatively that the intermediate phase between phases V and I of Na_2SO_4 is a pretransitional region where the skeleton structure is nearly the same as in phase V, but where there has been some rearrangement of atoms, i.e., an onset of rotation of sulfate anions. There is a need for more experiments such as Raman scattering and x-ray measurements to obtain a better microscopic understanding of the pretransition.

After passing through the pretransition region, sodium sulfate transforms to phase I in a sluggish manner at the ordinary heating rate of 10 °C/h, but the sluggishness diminishes at the slow heating rate, as mentioned in the preceding section. However, the conductivity appears to change in steps near the T_2 transition (see Fig. 6). These small jumps vary in position and in size from sample to sample.

After the V→I transition at 241 °C, the conductivity values are always larger than those of subsequent thermal cycles, and are abnormal (until 20–30 °C above T_2) in the sense that they are not well described by the Arrhenius equation (see Figs. 2–4). This means that the phase I occurring at the initial heating process is slightly different from the phase I of subsequent thermal cycles, which may be the main reason why the conductivity in the intermediate phase II appears differently on the first cooling compared with subsequent cooling cycles. Brodale and Giauque[4] have mentioned that Na_2SO_4 may contain many nuclei of phase V even if it is held at temperatures in which phase I is stable. Saito *et al.*,[10] from their DTA analysis, have also suggested that nuclei of phase V may remain over the whole temperature range on initial heating and cooling. At the present stage, however, the existence of predecessor nuclei in the transformed structure is not clear. Our macroscopic conductivity measurements cannot provide any strong evidence for or against this hypothesis.

In summary, the major V→I transition is characterized by a long stabilization time, a stepwise response, and an incomplete transition. The structural transition is a major one, as the crystal structures of phases V and I are very different,[13,14] and has to involve large displacements of cations and anions together with rotations of the anions. The atomic displacements at T_2 may occur abruptly but in progressive stages and by relatively small amounts in each stage or, alternatively, different regions of the crystal may successively change phase. In other words, the V→I transition involves such a drastic alteration in crystal structure that the changes cannot occur all at once, no matter how slowly the transition takes place. Thus the transition cannot be described in the usual terms; it is neither first nor second order in character, as the transition is not thermally reversible. There can be no soft mode driving the transition, nor is it of the conventional order-disorder type.

Except for the first heating cycle of a fresh Na_2SO_4(V) crystal, the sequences of transitions are well represented by III→I on heating and I→II→III on cooling. Although sodium sulfate is not a good fast ion conductor, the III→I transition clearly belongs to the type-I transition of fast ion conductors, as classified by Boyce and Huberman,[21] even though there is an intermediate phase II in a narrow temperature region on cooling. In the type-I transition (well-known prototype materials are AgI and Li_2SO_4), the phase changes through a first-order transition involving a rearrangement of the immobile-ion sublattice and disordering of the mobile-ion sublattice.

The conductivity measurements in the high-temperature phase of polycrystalline sodium-sulfate-based systems with various dopants have been well studied[24–26] and it has been assumed that the dominant intrinsic defects are most likely cationic Frenkel defects. Hence, the high-temperature phase (I) of Na_2SO_4 is considered to show ionic mobility by simple physical sublattice expansion,[12,26] by Na^+ ion vacancies on normal lattice sites,[24–26] and by interstitial Na^+ ions.[19,25] In our single-crystal conductivity data, the III→I transition exhibits a sharp jump by a factor of 5 in conductivity along all three orthogonal directions (for powder samples the factor is higher; from 7 in our case, to 10 in Ref. 26). This must be directly associated with the large volume expansion (4%) at the III→I transition. The relatively lower conductivities of phases I and III as compared with phase V (excluding the *b* axis) is consistent with their more compact crystal structure. Our results concerning the peculiarities of phase V prove that the relative openness of the crystal lattice in certain directions is one of the most important factors in ionic conduction.

V. CONCLUSIONS

This first detailed study of the conductivity of oriented single crystals of the ionic conductor Na_2SO_4 has revealed new information about its structural transitions and the nature of the conductivity. The conductivity in the stable room-temperature orthorhombic phase (V) is very anisotropic, being restricted largely to the (010) plane. Analysis of the crystal structure reveals open tunnels in the [101] and $[10\bar{1}]$ directions that form an interconnected network in the (010) plane. These provide suitable diffusion paths for Na^+ ions. The thermally irreversible transition to hexagonal phase I at 241 °C is sluggish, occurs in a stepwise fashion, is possibly incomplete, and is apparently accompanied by a pretransition region. The microscopic details of this major structural change are as yet unknown but the open structure of phase V clearly facilitates the large anion displacements that must occur. The transition is not of a conventional type, as are, for example, soft-mode or order-disorder transitions, and may not be properly described as first or second order.

The conductivities in the [100] and [001] directions decrease when phase I is entered and the conductivity becomes essentially isotropic, consistent with the tighter crystal structure. On cooling, a transition to phase II occurs at 234 °C before a further transition at 229 °C to the metastable phase (III) of orthorhombic symmetry. On further heating there is a direct transition at 249 °C from phase III to a true phase I. Apart from the existence of phase II, this transition may be characterized as a fast ion conductor type-I transition.

ACKNOWLEDGMENTS

We thank H. J. Labbé for technical assistance and Y. Le Page for the x-ray orientation of Na_2SO_4 crystals.

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