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Structural and nonstructural factors in fast ion conduction in Ag_2SO_4 at high pressure

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The ac electrical conductivity of Ag_2SO_4 has been measured as a function of pressure up to 52 kbar and in the temperature range 300–1000 K. At low P, the orthorhombic to hexagonal transition, with positive $\Delta V_{\text{ortho}\rightarrow\text{hex}}$, is accompanied by a large increase in conductivity suggesting dominant control of lattice volume on fast ion conduction. The high-P conductivity data confirm the maximum in the orthorhombic-hexagonal P-T phase boundary at ~16 kbar as reported in an earlier differential thermal analysis study. However, at high P, where $\Delta V_{\text{ortho}\rightarrow\text{hex}}$ is negative, the persistent but muted increase in conductivity across the orthorhombic to hexagonal boundary suggests that P induced changes in nonstructural factors dominate in controlling conduction. The σ-P data show a pronounced trough between 15 and 20 kbar which virtually disappears at the orthorhombic to hexagonal transition at ~720 K. Above 720 K, the decrease in σ becomes more gradual with P. The activation energy, Q_c, for ionic conductivity in the hexagonal phase is effectively independent of P up to ~10 kbar followed by a precipitous drop at 16 kbar with complete recovery at ~30 kbar. The coincidence of the minimum in Q_c and the maximum in the orthorhombic-hexagonal P-T phase boundary is discussed in terms of the deformability of the Ag^+ ion and its effects on bond strength and the thermodynamic constraints of Clapeyron slopes, respectively. The activation volume for both the orthorhombic and hexagonal phases is strongly T dependent for $P<16$ kbar but T independent for $20<P<52$ kbar. The results are compared with previously reported results of parallel studies on Na_2SO_4 and $AgTlSO_4$. [S0163-1829(97)08930-3]

I. INTRODUCTION

Ag_2SO_4 is one of a number of sulfates, viz. Li_2SO_4, Na_2SO_4, and $AgTlSO_4$, etc., along with iodides and Li_2MCl_4 spinels that undergoes a solid-solid phase transition accompanied by a large jump, up to a factor of 10^4, in ionic conductivity. The abrupt jump in conductivity accompanying the structural change at the transition into the fast-ion conducting phase is a paradigm for a structure-property relation. Structural factors can involve coordination geometry/number, face-sharing sites, and lattice disorder. On the other hand, nonstructural factors such as lattice "free volume" and bottleneck size can also contribute significantly. Free volume is understood as the unoccupied space or the interstitial volume and bottleneck size is understood as the constriction between two interstices in any given lattice. Although structure plays a role in determining these factors, it does not singularly control "free volume" and bottleneck size. Examples of isomorphous compounds with different "free volumes" and bottleneck sizes are α-Ag_2SO_4 and Na_2SO_4-I, space group $P6_3/mmc$, and TlCl, TlBr, and α-TlI, space group $Pm3m$. Other nonstructural factors that affect fast-ion conduction in solids are activated ion concentration, ion-ion interaction or bonding characteristics, vibrational amplitudes of neighboring ions, lattice compressibility or resiliency, ion size, polarizability of the oppositely charged ion, the electron configuration of the mobile ion and its polarizability along with any rotational motion/frequency of complex ions in the structure. Any one of these structural or nonstructural factors can by itself or in concert with another play a dominant role in fast ion transport. One of the more promising avenues to probe into the mechanism of ion transport is, in our view, to explore the relationship between ion conductivity and these factors via solid phase transitions where the transition to the high temperature phase is accompanied by a significant jump in conductivity.

The effect of pressure on a solid undergoing a structural transition to a fast-ion conducting structure can manifest itself on any nonstructural factor. For example, the dependence of conductivity on hydrostatic pressure, P, provides insight to the dependence of conductivity on lattice "free volume." Free volume is the critical fraction of the total lattice volume, V, of the solid with respect to the conduction process and it is also the fraction of the total lattice volume that is most susceptible to change by pressure. The effect of P on V of a solid will consequently reflect itself on the "free (interstitial) volume." From the relation $V \propto 1/P$, we expect that conductivity decreases as the "free volume" decreases with increasing pressure. Also, the pressure dependence yields an "activation volume" which is a measure of the volume change required for the motion of the mobile ion through the transport bottleneck. It therefore is a measure of the extent to which the lattice must expand to facilitate mobile ion passage through the bottleneck or window. The bottleneck size can also be reflected in the activation energy barrier separating a set of energetically favorable sites that the ion must surmount.

This paper focuses on the temperature and pressure de-

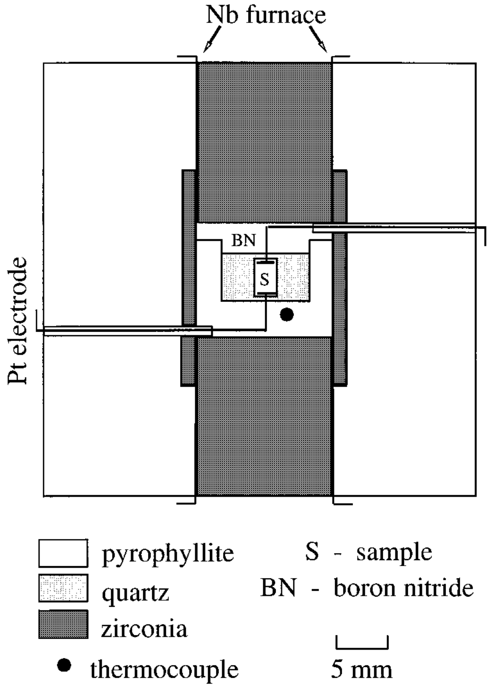

FIG. 1. Cross sectional view of pressure cell configured for high-temperature conductivity measurements.

pendence of the electrical conductivity of the two structural forms of Ag_2SO_4, low-temperature β-Ag_2SO_4 orthorhombic space group $Fddd$ and high-temperature α-Ag_2SO_4 hexagonal space group $P6_3/mmc$. Of special interest are Na_2SO_4-I and α-Ag_2SO_4 which are isomorphic and with similar unit cell dimensions.[1,2] The existence of these two isomorphic compounds with a common SO_4^{2-} sublattice or framework presented us with an opportunity to view the paradigm of a structure-property relation from another perspective with respect to earlier conductivity studies on Na_2SO_4 at high pressures[3] and on $(Na,Ag)_2SO_4$ at 1 atm.[4]

From the isobaric conductivity-temperature plots, we obtain the $\alpha \leftrightarrows \beta$ transition temperatures T_t for Ag_2SO_4. With T_t as a function of pressure, we construct the subsolidus phase diagram for Ag_2SO_4.

II. EXPERIMENT

The high-pressure experiments were carried out in a 1000 ton cubic anvil press. Detailed descriptions of the apparatus[5] and pressure calibration[6] have been given elsewhere. The prepared pyrophyllite pressure cell, as shown in cross section in Fig. 1, was placed in a vacuum oven at 118 °C to remove any adsorbed water for several days prior to loading in the press. At high pressures, the temperature was controlled by Joulean heating of a cylindrical Nb foil furnace and measured with a PtPt-10%Rh thermocouple with corrections applied for the pressure effect on the emf.[7] Separate experiments using pressure cells of similar configuration in which temperature gradients were measured showed that the temperatures of the thermocouple and the sample differ by less than 1 K. Pt electrodes, each constructed from a single length of wire, contacted the disk-shaped (2.0 mm diameter, 1.6 mm thick), precompacted, polycrystalline sample which was contained in a SiO_2 cup [$\sigma_{SiO2} \sim 10^{-14}$ $(\Omega\ m)^{-1}$ measured at 22 °C and 1 atm].

Isobaric impedance measurements in three separate experiments were made at a total of 18 pressures in the pressure range 6.9–51.5 kbar and in the temperature range 297–1093 K at 5–20 K intervals. Impedance was measured at 1 kHz using a Stanford Research LCR meter (model 720) with a measured accuracy of better than 0.1%. Ten measurements were taken 2–3 min after the sample temperature had stabilized and were averaged.

X-ray patterns were recorded at room temperature on pre- and postrun powders with a Rigaku powder diffractometer to confirm the reversibility of the high P,T transformations.

III. RESULTS AND DISCUSSION

The fundamental thermodynamic equation for the conduction process in a system of fixed composition is given by the free energy of activation, $\Delta G^{\ddagger}$,

$$d\Delta G^{\ddagger} = -\Delta S^{\ddagger} dT + \Delta V^{\ddagger} dP, \tag{1}$$

yielding $\Delta V^{\ddagger} = (\partial \Delta G^{\ddagger}/\partial P)_T$, the characteristic activation volume and $\Delta S^{\ddagger} = -(\partial \Delta G^{\ddagger}/\partial T)_P$, the characteristic activation entropy as limiting cases for constant T and P, respectively. With the Arrhenius-type kinetic expression for the ionic conductivity,

$$\sigma = (nq^2 d^2 \nu \gamma / kT) e^{(-\Delta G^{\ddagger}/kT)}, \tag{2}$$

we obtain the activation volume

$$\Delta V^{\ddagger} = -RT(\partial \ln(\sigma T)/\partial P)_T + RT(\partial \ln(nq^2 d^2 \nu \gamma)/\partial P)_T, \tag{3}$$

where n is the activated mobile ion concentration, q the ion charge, d the intersite distance, ν the jump frequency, γ the geometry factor, and k and R are fundamental constants. The first term is obtained directly from the measured pressure dependence of conductivity. The second term, which is usually negligible relative to the first[8] can be simply represented by $\beta\Gamma$, β the isothermal compressibility and Γ the Grüneisen parameter. Equation (2) is cast into simpler form:

$$\sigma T = \sigma_o e^{(-\Delta G^{\ddagger}/RT)} = \sigma_o [e^{(\Delta S^{\ddagger}/R)} e^{-(\Delta H^{\ddagger}/RT)}] \tag{4}$$

or

$$\sigma T = \sigma_o' e^{(-Q_c/RT)}, \tag{5}$$

where $\Delta H^{\ddagger} = Q_c$ (i.e., the activation enthalpy equals the apparent activation energy for conduction which may include both defect formation enthalpy and mobility contributions) and $\sigma_o' = \sigma_o e^{(\Delta S^{\ddagger}/R)}$.

On the basis of Eq. (5), experimental data for the T dependence of the conductivity of Ag_2SO_4, plotted as $\ln(\sigma T)$ vs T^{-1} for seven selected pressures are given in Figs. 2(a) and 2(b) on heating and on cooling to illustrate the behavior. The orthorhombic to hexagonal transformation on heating is accompanied by an abrupt increase in conductivity with the lower pressure data showing a more pronounced jump at the transformation. The pressure dependence of the transformation temperature on heating for all 18 pressures investigated is shown in Fig. 3 in comparison with the orthorhombic-

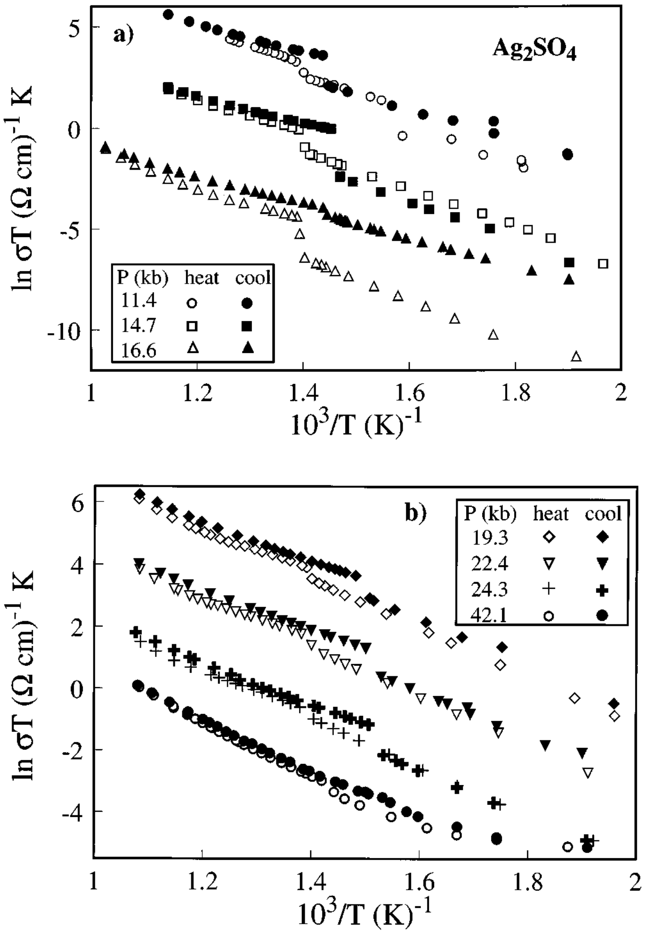

FIG. 2. Isobaric plots of $\ln(\sigma T)$ vs $T(\mathrm{K}^{-1})$ at 11.4, 14.7, and 16.6 kbar in (a) and at 19.3, 22.4, 24.3, and 42.1 kbar in (b) on heating and cooling. Each pressure data set (i.e., both heat and cool data) have been vertically shifted $+3$, 0, -4, $+4$, $+2$, 0, and -1 $\ln(\sigma T)$ units, respectively, for clarity. The true isothermal pressure dependence of conductivity is shown in Fig. 5.

hexagonal phase boundary determined at 1 atm by electrochemical methods,[9] conductivity,[10–12] DSC/DTA,[10–12] and at high pressure by DTA.[13] Our high-pressure conductivity data are in very good agreement with the 1 atm conductivity as well as the high-pressure DTA results, which are extrapolated as the dashed line in Fig. 3 for comparison purposes. The high pressure conductivity data confirm the change in sign of the slope of the phase boundary at approximately 16 kbar as first reported by Pistorius.[13]

Many changes in slope and most changes in the sign of the slope of a P-T phase boundary are indicative of a triple point [e.g., III-IV-VI triple point in Na_2SO_4 (Ref. 14) and I-III-IV triple point in Li_2SO_4 (Ref. 15)] and therefore an extremum in any solid-solid or solid-liquid phase boundary is unusual. At a maximum, as at $P \sim 16$ kbar in the P-T phase diagram of Ag_2SO_4 shown in Fig. 3, the volume change accompanying the structural transition, ΔV_t, reverses sign from positive (for $P < 16$ kbar) to negative (for $P > 16$ kbar) as P increases. If real, this implies, on the basis of the Clapeyron equation

$$dT/dP = T\Delta V_t/\Delta H_t, \tag{6}$$

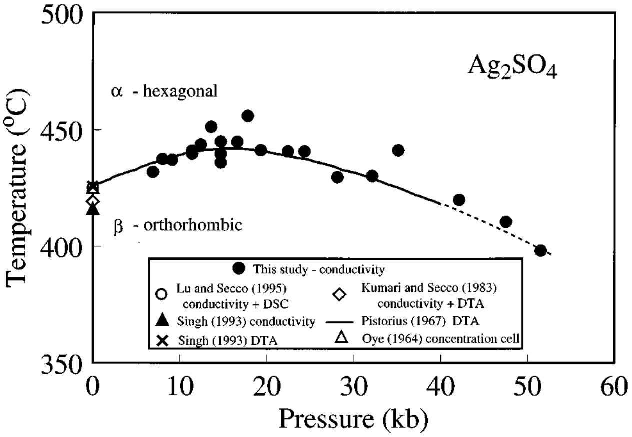

FIG. 3. Pressure dependence of the β-Ag_2SO_4-α-Ag_2SO_4 structure transformation temperature on heating for all 18 pressures investigated in this study compared with the high-pressure DTA results of Pistorius[13] and several determinations at 1 atm.

where ΔH_t is the enthalpy change accompanying the transition, that ΔV_t or ΔH_t must change sign. From the high-pressure DTA study,[13] which suggests that ΔH_t for the endothermic orthorhombic to hexagonal transition does not change sign at 16 kbar, we conclude that $\Delta V_t > 0$ for $P < 16$ kbar but $\Delta V_t < 0$ for $P > 16$ kbar. This could be simply explained by a structural phase boundary with a large dT/dP value (i.e., nearly vertical in P-T space) intersecting the boundary shown in Fig. 3 at 16 kbar. The large dT/dP value of a phase boundary at any extremum is required by the following generalized constraint of conservation of any thermodynamic property in a closed loop around any triple point of phases I-II-III:

$$\Delta X_{\text{I-II}} + \Delta X_{\text{II-III}} + \Delta X_{\text{III-I}} = 0, \tag{7}$$

where X is volume V, enthalpy H, or entropy S and the direction of the loop, indicated by the subscript order, must be constant. When combined with the Clapeyron equation (6), the triple point thermodynamic conservation equation (7) can be written in terms of the local slopes of the P-T phase boundaries between phases I, II, and III as

$$\begin{aligned}\Delta X_{\text{I-III}} = {} & [(dT/dP)_{\text{I-III}}][(dT/dP)_{\text{II-III}} - (dT/dP)_{\text{I-II}}] \\ & \times \Delta X_{\text{I-II}}/[(dT/dP)_{\text{I-II}}][(dT/dP)_{\text{II-III}} \\ & - (dT/dP)_{\text{I-III}}].\end{aligned} \tag{8}$$

We apply Eq. (8) to Ag_2SO_4 and designate the low-temperature phase as I, the low-pressure–high-temperature phase as II, and the high-pressure–high-temperature phase as III. On the basis that $(dT/dP)_{\text{I-II}} \approx -(dT/dP)_{\text{I-III}}$ at an assumed 16 kbar triple point, we make the assumption that $\Delta V_{\text{I-II}}$ and $\Delta V_{\text{I-III}}$ are both small [since $(dT/dP)_{\text{I-II}}$ and $(dT/dP)_{\text{I-III}}$ are both ≈ 0 near 16 kbar] and that $\Delta V_{\text{I-II}} \approx -\Delta V_{\text{I-III}}$. Therefore, Eq. (8) can be simplified and rewritten as

$$\begin{aligned}(dT/dP)_{\text{II-III}} = {} & [2(dT/dP)_{\text{I-II}}(dT/dP)_{\text{I-III}}]/[(dT/dP)_{\text{I-II}} \\ & + (dT/dP)_{\text{I-III}}].\end{aligned} \tag{9}$$

From the denominator of Eq. (9), the near vanishing sum of two phase boundary slopes of approximately equal magnitude but opposite in sign requires the slope $[(dT/dP)_{\text{II-III}}]$ of a new structural phase boundary constructed at 16 kbar to be very large. From this point of view, it is interesting to compare the phase diagrams of Ag_2SO_4 and Na_2SeO_4 .[16] The low-temperature structure of Na_2SeO_4 is orthorhombic space group $Fddd$ and the high-temperature structure has been suggested[17] to be similar to the structure of Na_2SO_4-I, paralleling the low- and high-temperature structures, respectively, of Ag_2SO_4 . The temperature of the orthorhombic-hexagonal phase boundary for Na_2SeO_4 increases with pressure but is concave toward the pressure axis and reaches a triple point at 36 kbar. This is exactly the pressure where the slope of the Na_2SeO_4 orthorhombic-hexagonal phase boundary appears to change sign. For the reasons explained above and summarized in Eq. (9), the phase boundary between the low-pressure–high-temperature and high-pressure–high-temperature Na_2SeO_4 structures has a large dT/dP value of 10 °C/kbar. These structural similarities between Ag_2SO_4 and Na_2SeO_4 prompt the question of the possibility of a new structural, first order phase transformation for Ag_2SO_4 in the 16 kbar region at high temperature. To our knowledge, no crystal structure data are available for Ag_2SO_4 at pressures higher than 1 atm. According to Pistorius,[13] however, ''it is possible but improbable that the maximum is due to a new high-pressure phase intervening at ~16 kbar'' since no DTA indication was found. With regard to the DTA results, the importance of a large $(dT/dP)_{\text{II-III}}$ discussed above is twofold: (i) from the Clapeyron equation (6), $\Delta H_{\text{II-III}} \approx 0$ which makes DTA an insensitive technique to any possible phase change; and (ii) the near vertical attitude of a possible II-III boundary for Ag_2SO_4 would make traversing it virtually impossible during isobaric temperature runs as in the Pistorius study [note, however, that isothermal pressure runs would not be superior to isobaric temperature runs in this case for the reason stated in (i) above]. We conclude that the absence of any DTA indication for a structural phase boundary intersecting the low-pressure orthorhombic-hexagonal phase boundary at approximately 16 kbar is insufficient evidence for precluding it (consequently, a high-pressure x-ray crystallography study is planned). However, despite having just argued for its possible existence, from arguments that will follow, we do not expect to find any structural differences for Ag_2SO_4 between the low- and high-pressure regions at temperatures above approximately 450 °C.

At the transition in the low-pressure region at $P < 16$ kbar, the jump in conductivity may be easily understood in terms of an increase in structure ''free'' volume where $\Delta V_t \sim 3-4.5\ \%$.[13] However, the increase in conductivity at the transition in the high-pressure region at $P > 16$ kbar as shown in Fig. 2(b), albeit somewhat muted compared to the low-pressure behavior, cannot be similarly explained since $\Delta V_t < 0$.

A plot of Q_c for the high-temperature phase of Ag_2SO_4, obtained from measurements on heating, versus pressure is given in Fig. 4 and a schematic of the Q_c trends for Ag_2SO_4, Na_2SO_4,[3] and $AgTlSO_4$ (Ref. 18) is shown for comparison in the inset figure. The high-pressure Q_c data are from three separate experiments denoted by the different filled symbols. Apart from the high Q_c value of 71 kJ/mol at 11.4 kbar (which we include only with skepticism in observing completeness of data reporting since it was the first heat/cool cycle of that experiment and the sample may have undergone some annealing as have samples of $AgTlSO_4$ in a previous study[18]), the pressure dependence of Q_c for Ag_2SO_4 is anomalous in comparison with the isomorphous Na and mixed AgTl analogue sulfates. At approximately 5–8 kbar, Q_c drops precipitously toward a low value of 28–33 kJ/mol at ~16 kbar and then recovers to a value of ~60 kJ/mol at ~30 kbar. Above 30 kbar, Q_c for Ag_2SO_4 follows a similar, monotonic, linear pressure dependence and is similar in magnitude to the hexagonal phase of Na_2SO_4 and the high-temperature $AgTlSO_4$, which is also expected to be hexagonal.[18] The dotted line in Fig. 4 between 12 and 29 kbar, bridging the drop in Q_c for Ag_2SO_4 , shows that the linear extrapolation of the high-pressure trend can be reasonably fitted to the low-pressure data. From the general similarity of the pressure dependences of the Q_c for all three sulfates in Fig. 4, we expect the high-pressure–high-temperature structure of Ag_2SO_4 to be hexagonal as well. The striking departure of Q_c for Ag_2SO_4 in the 8–30 kbar range from linearity, and in particular, the initial decrease of Q_c with increasing pressure up to 16 kbar, was consistently observed in all three experiments. A decrease in Q_c with pressure is uncommon for ionic conduction if a simple volume-controlled mechanism of conduction is adopted. We therefore look to other nonstructural factors that may facilitate the transport of the mobile Ag^+ ion in a reduced volume lattice.

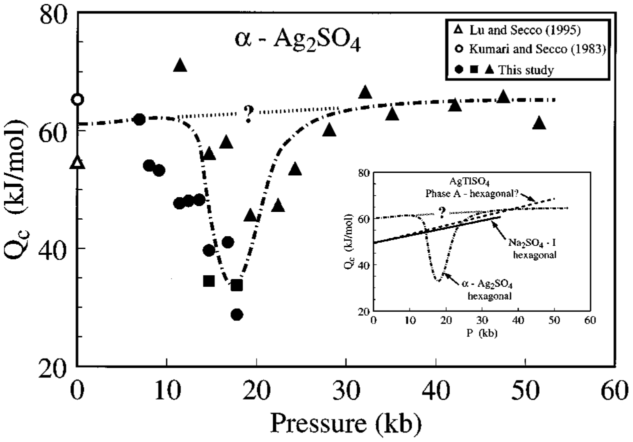

FIG. 4. Activation energy vs pressure calculated for the high-temperature α-phase from $\ln(\sigma T)$ vs $T(K^{-1})$ data on heating. The inset figure shows the schematic trend of Q_c for α-Ag_2SO_4 in comparison with isomorphous Na_2SO_4-I and phase A of $AgTlSO_4$ (suspected hexagonal). The dotted line is a linear extrapolation of the high-pressure Ag_2SO_4 data across the pressure region where Q_c reaches a minimum.

In a recent study,[11] the distinct conductivity behavior of Ag^+ and Tl^+ with regard to cation conductivity relative to other isovalent cations in a common SO_4^{2-} sublattice and common structural framework was interpreted in terms of polarizability linked to their closed outer shell configuration, viz. $4d^{10}$ and $5d^{10}6s^2$, respectively. The high polarizability of Ag^+, $\alpha_{Ag^+} = 2.4$ Å^3,[19] can affect ion-ion interaction or bonding. Since the activation energy for ionic migration or transport is the sum of three energies, i.e., $Q_c = E_e + E_s$

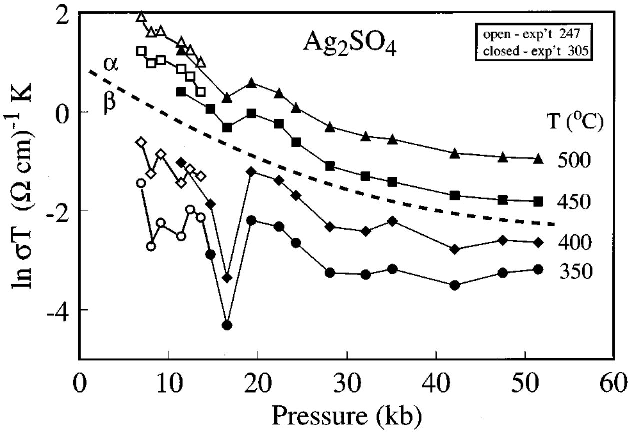

FIG. 5. Isothermal plots of ln(σT) vs pressure on heating from two different (low pressure, open symbols; high pressure, closed symbols) experiments. The dashed line separates the data into two sets corresponding to the α- and β-Ag_2SO_4 phase regions.

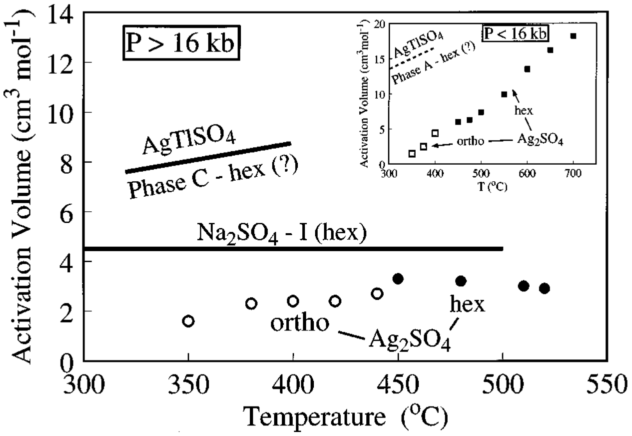

FIG. 6. Activation volume vs temperature for high- and low-pressure regions shown in the main and inset figures, respectively. The low activation volumes for Ag_2SO_4 derived from high-pressure data are compared with Na_2SO_4-I and the high-temperature–pressure phase C of $AgTlSO_4$ and are contrasted with the high activation volumes for Ag_2SO_4 derived from low-pressure data.

$+E_r$, where E_e is the Coulombic attraction $(+\ -)$ between the cation and its anion surroundings (i.e., Ag^+-$SO_4{}^{2-}$), E_r is the mobile ion-ion repulsion energy $(+\ +$, i.e., Ag^+-$Ag^+)$, and E_s is the elastic strain (nonelectrostatic) energy for a cation passing through the bottleneck,[20] a pressure-induced reduction in any one or more components could give rise to an overall pressure-induced decrease in Q_c. Recently, Rosenberg *et al.*[21] reported on the relationship between Ag^+ electron cloud deformability on Ag^+-I^- bonding in host KI from stress-induced frequency shifts in IR-active modes in the vibrational spectrum caused by application of a dc electric field. Their study has established firmly the significant electronic deformability of the Ag^+ ion and its unusual effect on Ag^+-I^- bond strength. Using a harmonic perturbed shell model, adjusted for anharmonic effects due to site specific electric field-induced local strains around the Ag^+ defect, Rosenberg *et al.*[22] had predicted earlier that a decrease in Ag^+ [on (200) sites] -I^- [on (100) sites] separation would cause a decrease in the (200)-(100) longitudinal force constant. This is an unusual response to pressure in any lattice that is characterized by repulsive-dominated interatomic potentials. In light of pressure-induced mode softening evident in Ag^+-defect hosted KI, we speculate that the negative pressure dependence of Q_c for Ag_2SO_4 in the range 8–16 kbar presented here, may be a result of pressure-induced weakening, possibly due to increased covalency, of the Ag^+-$SO_4{}^{2-}$ bonds. In this context, Wuensch[23] has shown that the ion transport process does not depend solely on the geometry of the anion array but it is also affected by the bonding characteristics. A reduction in Ag^+-$SO_4{}^{2-}$ bond strength would lead to a reduction in E_e and as a consequence, a decrease in Q_c. The overall effect of a decrease in Ag^+-$SO_4{}^{2-}$ bond strength is an increase in lattice compressibility. Pressure reduced lattice volume and pressure reduced bond strengths are antagonistic (i.e., hindering and enhancing, respectively) effects on ionic conduction. The minimum in the pressure dependence of Q_c may therefore reflect the competition of these two effects and the relative dominance of one over the other.

The isothermal pressure dependence of the conductivity is shown in Fig. 5 for two temperatures in each of the β-orthorhombic phase (350 °C and 400 °C) and α-hexagonal phase (450 °C and 500 °C) regions. For all four isotherms, the conductivity decreases to a minimum at 16 kbar and then increases to a value larger than what would have been predicted by the extrapolated low-pressure dependence. This is consistent with enhanced conductivity caused by pressure-induced weakening of the Ag^+-$SO_4{}^{2-}$ bond. It is noteworthy that both sets of isotherms, below and above the orthorhombic to hexagonal transition, show the same feature but the effect is more pronounced in the orthorhombic region indicating a possible structure/bonding environment dependence of the deformability of the Ag^+ ion.

Activation volume was derived from the pressure dependence of the conductivity using the first term of Eq. (3) and is plotted versus temperature in Fig. 6 for the orthorhombic and hexagonal structures of Ag_2SO_4. For comparison, $\Delta V^{\ddagger}$ for the hexagonal phase of Na_2SO_4[3] and the high-temperature region (suspected hexagonal) of $AgTlSO_4$ (Ref. 18) is also plotted in Fig. 6. For Ag_2SO_4, the $\Delta V^{\ddagger}$ data plotted in the main body of Fig. 6 are for $P > 16$ kbar and the $\Delta V^{\ddagger}$ data plotted in the inset figure are for $P < 16$ kbar, as reported earlier.[24] For the high-temperature phase of Ag_2SO_4, the large $\Delta V^{\ddagger}$ values and their large positive T dependence below 16 kbar parallel the behavior for $AgTlSO_4$ while the small $\Delta V^{\ddagger}$ values and their T independence for the high-temperature phase of Ag_2SO_4 above 16 kbar parallel the behavior for Na_2SO_4-I. The similarity in the $\Delta V^{\ddagger}$ behavior of the high-temperature–high-pressure phase of Ag_2SO_4 and the hexagonal structure Na_2SO_4-I phase reinforces our suspicion of a similar structure for Ag_2SO_4 in the high-temperature region at $P > 16$ kbar. This interpretation, while in need of confirmation by *in situ* high P,T structural data, is consistent with both the Pistorius[13] and the Rosenberg *et al.*[21] results. Specifically, we do not anticipate a structure transformation at 16 kbar but the unusual maximum in the solid-solid boundary between the orthorhombic and hexagonal phases can be explained by pressure-induced changes in Ag^+-SO_4^{2-} bonding, most likely related to the deformability of the Ag^+ ion electron cloud. In essence therefore, Ag_2SO_4 can be pressure tuned to behave similarly to Na_2SO_4 despite the large difference in mass ($m_{Ag^+}/m_{Na^+}=4.70$), outer shell electron configuration (Ag^+-$4d^{10}$, Na^+-$2s^2p^6$), and moderate difference in ionic radius ($r_{Ag^+}/r_{Na^+}=1.11$).

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