Structural behaviour at the γ-β phase transition of Ag_3SI

LETTER TO THE EDITOR

Structural behaviour at the γ–β phase transition of Ag$_3$SI

D A Keen[1,2] **and S Hull**[2]

[1] Physics Department, Oxford University, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
[2] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 QX, UK

**Abstract**
Temperature-dependent powder neutron diffraction has been used to investigate the structure of the superionic compound Ag$_3$SI in the region of the γ–β phase transition at $T_{\gamma-\beta} = 157$ K. On cooling through $T_{\gamma-\beta}$ the structure changes from cubic to rhombohedral as the three silver ions per unit cell preferentially occupy six of the twelve sites which are randomly occupied in the cubic phase. This is accompanied by a slight distortion of the anion sublattice along one of the threefold axes. Cooling below $T_{\gamma-\beta}$ produces a further gradual ordering of the silver ions with each silver ion on a single site and an increased distortion of the anion sublattice. This behaviour is used to interpret the observed ionic conductivity of Ag$_3$SI and to resolve the ambiguity over the nature of the phase transition.

Ag$_3$SI is a superionic material with three distinct phases. At high temperature the α-phase exists in an α-AgI-type bcc structure with random occupation of sulphur and iodine ions over the 2(a) positions within space group $Im\bar{3}m$. Slow cooling through the α–β phase transition at 519 K results in an ordering of the sulphur and iodine ions over (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) positions and a lowering of symmetry to space group $Pm\bar{3}m$. At $T_{\gamma-\beta} = 157$ K, the β-phase transforms to the low-temperature γ-phase, which is characterized by a rhombohedral distortion of the anion sublattice within space group $R3$. The three cations within the unit cell are distributed over 24, 12 and 3 equivalent sites within the α-, β- and γ-phases respectively. The structures are described in detail in our previous paper [1] and the references contained therein.

The ionic conductivity is strongly temperature dependent (see figure 1 (top panel)). Within the γ-phase it rises by three orders of magnitude between 100 and 156 K and there is a sharp discontinuity at $T_{\gamma-\beta}$ followed by a further, more gradual, increase with increasing temperature in the β-phase [1]. The α-phase, when quenched to room temperature, has an ionic conductivity of $\sigma \sim 0.3$ Ω^{-1} cm^{-1} [2].

The specific heat changes at the two phase transitions of Ag$_3$SI show two different behaviours [3]. The β–α transition is of first order whereas the γ–β transition shows evidence for a λ-anomaly, indicative of a second-order phase transition. The latter is inconsistent with the discontinuity of the ionic conductivity at $T_{\gamma-\beta}$ and the phase transition has been described
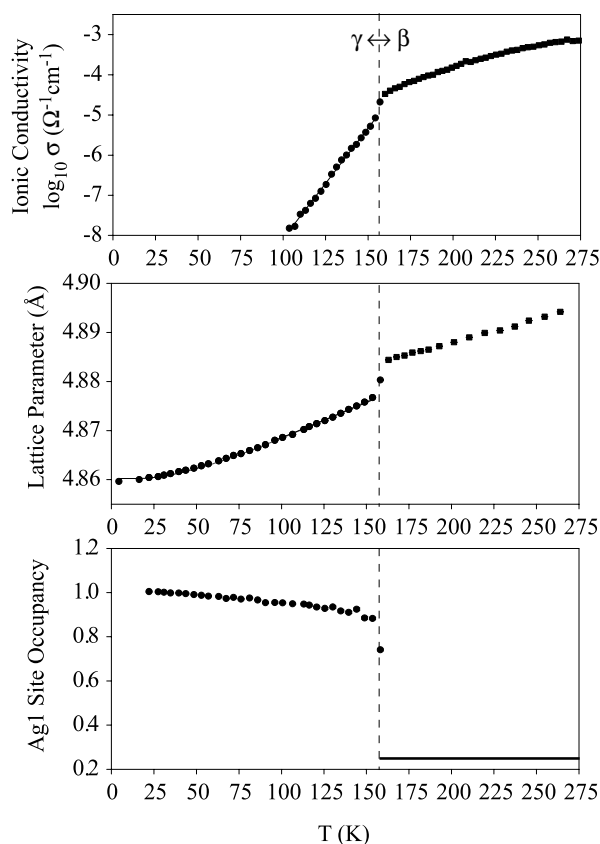
Figure 1. Plots showing the temperature dependence of (top) the ionic conductivity [1], (middle) the lattice parameter and (bottom) the site occupancy of the Ag1 site in Ag$_3$SI. The full line in the middle panel shows an Einstein model fit to the lattice parameter in the γ-phase. A 90° rhombohedral angle is assumed for the γ-phase and the Ag1 site is one of the four sets of threefold sites over which the cations disorder in the β-phase (see the text for details).

as first order, with significant second-order character [3]. Second-order behaviour should be seen in the temperature dependence of the crystal structure. The purpose of this letter is to characterize the γ–β phase transition fully using powder neutron diffraction and to resolve the apparent inconsistency between ionic conductivity and specific heat measurements.

Powder neutron diffraction measurements have been made on the GEM diffractometer at ISIS in fine temperature steps between 5 and 300 K using a helium cryostat and a sample contained in a thin-walled cylindrical vanadium container. The sample was fabricated in an identical manner to the sample used in [1], but annealed at 473 K for much longer (about six months). The data were measured for ~40 min at each temperature, in 5 or 10 K steps, starting at low temperature. The data treatment and methods for Rietveld profile refinements have been described previously [1].

Data at low temperature were refined using the fully ordered structure [1] in space group $R3$ with S^{2-} on 1(a) at (xxx) with $x \gtrsim 0$, I$^-$ on 1(a) with $x = \frac{1}{2}$ and Ag$^+$ on 3(b) at (xyz) with $x \sim 0.5$, $y \sim 0.9$ and $z \sim 0$ (Ag1). In addition, possible disordering of the cations onto different 3(b) sites which are also subsets of the partially occupied 12(h) sites in space group $Pm\bar{3}m$ in β-Ag$_3$SI (see below) was investigated. These are Ag2 with $x \sim 0.5$, $y \sim 0$ and

$z \sim 0.9$, Ag3 with $x \sim 0.5$, $y \sim 0$ and $z \sim 0.1$ and Ag4 with $x \sim 0.5$, $y \sim 0.1$ and $z \sim 0$ (see figure 2). Ag2 is equivalent to Ag1 with respect to the S^{2-} distortion in so far as they are both displaced away from the direction of the S^{2-} movement from (000) with identical Ag^+–S^{2-} bond lengths and Ag^+–S^{2-}–Ag^+ bond angles. Ag3 and Ag4 also have the same Ag^+–S^{2-} bond lengths and Ag^+–S^{2-}–Ag^+ bond angles but are displaced towards the direction of S^{2-} movement. Consequently the Ag^+–S^{2-} bond lengths are longer when Ag^+ are located on Ag1 or Ag2 sites than when located on Ag3 or Ag4 sites. Earlier high-resolution measurements show that the α-angle is very close to $90°$, with a value of $\alpha = 90.08(2)°$ at 5 K [1]. Since GEM has a lower $\Delta d/d$ resolution, and the small peak splitting could not be observed, a fixed α-angle of $90°$ was used for all refinements in the γ-phase. Indeed, when the unit-cell angle was allowed to vary, only slightly better fits with marginally significant values of $\alpha > 90°$ were obtained for the lowest-temperature data. At higher temperatures the deviations were not statistically significant and gave physically unrealistic values of $\alpha < 90°$. Data for β-Ag_3SI were refined in $Pm\bar{3}m$ with S^{2-} in 1(a) sites at (000), I^- in 1(b) sites at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and Ag^+ distributed randomly between 12(h) sites at $(x\frac{1}{2}0)$ with $x \sim 0.1$. In both phases anisotropic temperature factors were attempted, but they only proved stable in the β-phase. This is not entirely surprising given the increased complexity of the γ-phase structure compared to the structure of the β-phase and that the data at each temperature were only collected for a relatively short time.
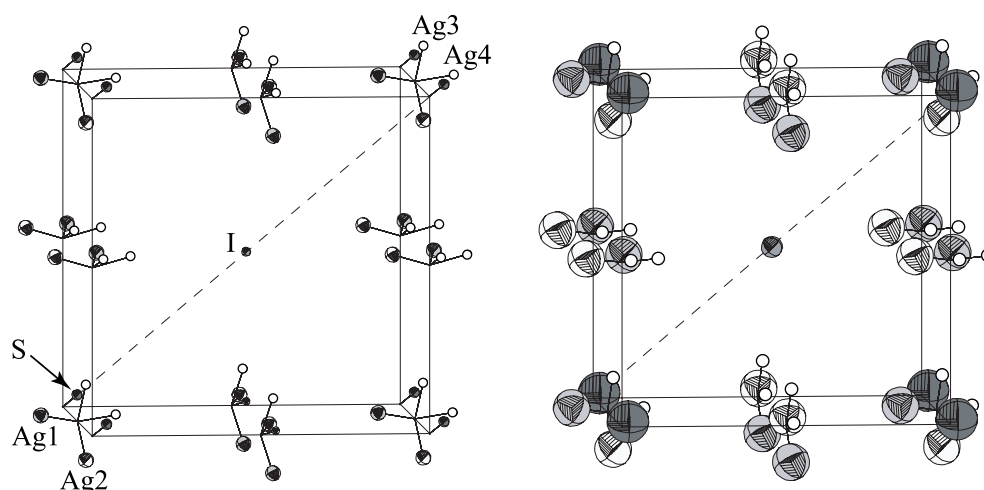

Figure 2. The crystal structure of γ-Ag_3SI at 22 K and 149 K. The positions of the Ag1, Ag2, Ag3 and Ag4 3(b) sites are indicated, although refinements show that the cation only resides in the Ag1 and Ag2 locations. Hence Ag3 and Ag4 sites are shown as open circles. Dashed lines indicate the unique 111 rhombohedral direction.

Figure 1, middle panel, shows the change of Ag_3SI lattice parameter with temperature. There is a discontinuous change in volume at $T_{\gamma-\beta}$ of $\Delta V/V = 0.47(4)\%$. In the β-phase the lattice parameter increases linearly with increased temperature whereas in the γ-phase the lattice parameter only increases linearly at higher temperatures. At lower temperatures the expansion is less rapid and the γ-phase expansion may be parametrized by a simple Einstein relation [4] yielding an Einstein temperature of $\theta_E = 111(5)$ K. This value for θ_E is close to $\theta_E = 130$ K determined from far-infrared measurements [5]. At the highest temperatures within the γ-phase, the refined models include a small occupancy of the Ag2 site

(see figure 1, bottom panel), suggesting that the cations are disordering between Ag1 and Ag2 sites. No cation density was found in Ag3 or Ag4 sites. Since the Einstein relation fits well for all temperatures, there is no evidence for an excess thermal expansion associated with this disordering. Such behaviour has been observed with increased Frenkel defect concentration in β-PbF$_2$ at the superionic transition [6]. However, such an effect would be unlikely in γ-Ag$_3$SI since, in contrast to the case for β-PbF$_2$, the disordering is between two sites with similar volumes.

Figure 3 shows the changes of atom positions and temperature factors in Ag$_3$SI as functions of temperature. There is a pronounced, but smoothly varying change in the position of the S^{2-} ion away from (000) as the temperature is lowered within the γ-phase. At 25 K the S^{2-}
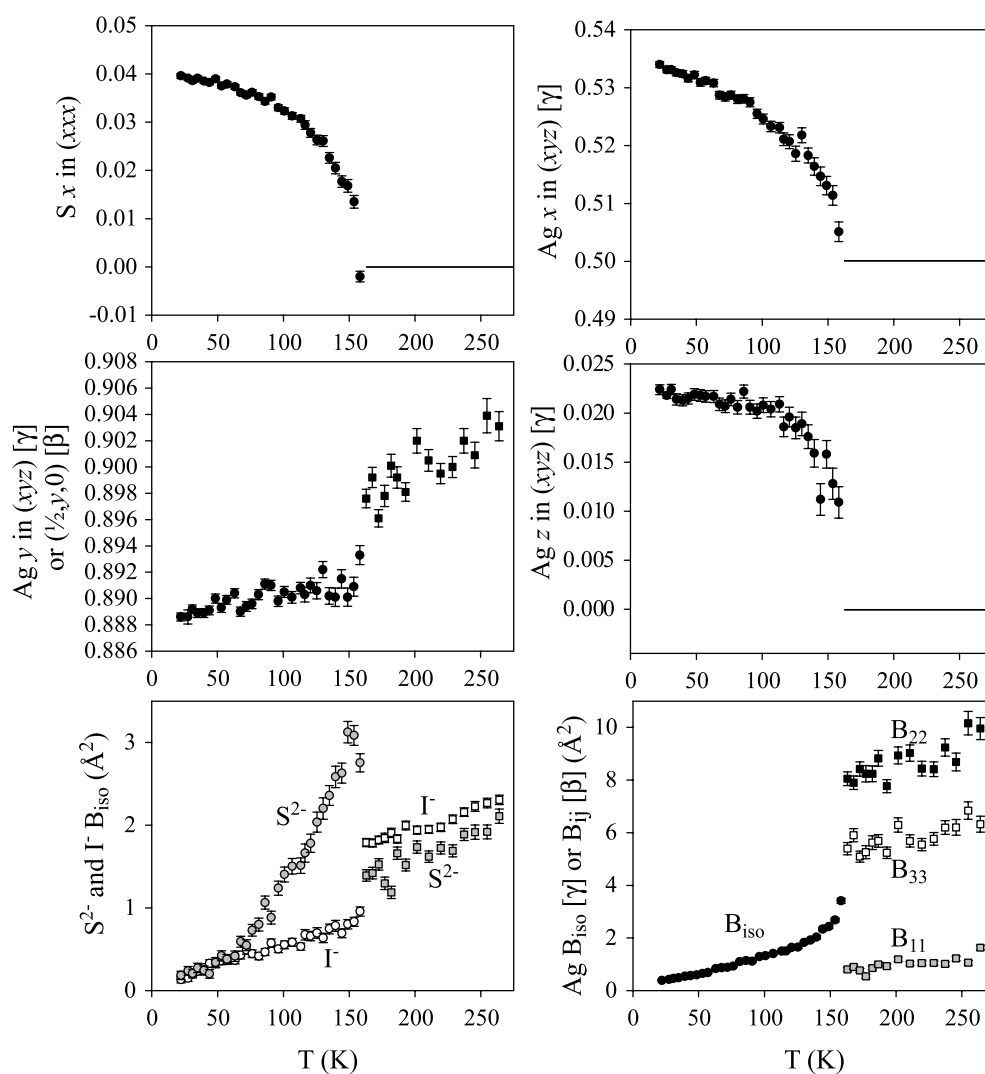
Figure 3. Plots of the temperature dependence of the internal structural parameters of Ag$_3$SI. In these plots the Ag$^+$ site in β-Ag$_3$SI is shown as $(\frac{1}{2}, y, 0)$. Squares and circles denote data within the β-phase and γ-phase respectively.

ion has moved 0.333 Å away from its ideal (000) site. Similar changes in the cation x- and z-positions and a small change in the cation y-position accompany this distortion. There is a large increase in the S^{2-} temperature factor with increased temperature within the γ-phase, achieving significantly larger values than that of I^-. The S^{2-} temperature factor actually decreases on transforming to β-Ag$_3$SI. Despite the fact that the rhombohedral splitting could not be resolved, the correlation between the S^{2-} positional parameter x and the S^{2-} isotropic temperature factor in the refinements was not significant. This, and the fact that the thermal displacements are not so large as to lead one to question the validity of the refined model, shows that the temperature dependence of the observed distortion and thermal displacements are robust and reflect the true response of the structure. The Ag^+ temperature factor also increases significantly within the γ-phase with increased temperature. In contrast it is strongly anisotropic in the β-phase, reflecting the disordered distribution of cations in β-Ag$_3$SI, and shows little temperature dependence.

It is now possible to understand the γ–β phase transition. The discontinuous change at $T_{\gamma-\beta}$, as seen in the ionic conductivity, the lattice parameter and the ordering of cations onto a subset of the twelve available β-phase sites, is strong evidence for the first-order character of the phase transition. This redistribution of cations destabilizes the anion lattice as seen in the large S^{2-} temperature factors just below $T_{\gamma-\beta}$. However, just below $T_{\gamma-\beta}$ the cations are not fully ordered and a small fraction ($\sim$10%) remain on Ag2 sites. As the temperature is lowered further, this Ag2 occupancy gradually reduces and the anion sublattice gradually becomes more distorted until the cations are fully ordered on Ag1 sites at the lowest temperatures. This ordering, which has second-order character, may be distinct from the first-order changes at $T_{\gamma-\beta}$. In addition, the fact that the γ-phase is partially disordered just below $T_{\gamma-\beta}$ may explain why the observed entropy change at $T_{\gamma-\beta}$ is lower than the $R\ln 4$ expected for a transition from a fully ordered γ-phase to a fully disordered β-phase with four sites per cation [3]. The observed value of $\sim$0.5$R\ln 4$ would be consistent with a transition between a phase with four sites/cation (β-Ag$_3$SI) to one with two sites/cation (i.e. the γ-phase when the cations are fully disordered between Ag1 and Ag2 sites).

Similarly, the number of mobile ions in both phases may explain the differences in the temperature dependence of the ionic conductivity in the γ- and β-phases. In the γ-phase, the conductivity at low temperatures is low because the structure is fully ordered. However, as the temperature is increased, there is a gradual disordering of cations between Ag1 and Ag2 sites in the γ-phase and these cations now contribute to the conduction. Hence the ionic conductivity rises rapidly in the γ-phase. In the β-phase, the cations are fully disordered and, since all may conduct, the conductivity is high and the change in conductivity with increased temperature is not as rapid as in the γ-phase.

References

[1] Hull S, Keen D A, Gardner N J G and Hayes W 2001 *J. Phys.: Condens. Matter* **13** 2295
[2] Chiodelli G, Magistris A and Schiraldi A 1979 *Z. Phys. Chem., NF* **118** 177
[3] Hoshino S, Sakuma T and Fujii Y 1979 *J. Phys. Soc. Japan* **47** 1252
[4] David W I F, Ibberson R M and Matsuo T 1993 *Proc. R. Soc.* **442** 129
[5] Brüesch P, Beyeler H U and Strässler S 1982 *Phys. Rev.* B **25** 541
[6] Goff J P, Hayes W, Hull S and Hutchings M T 1991 *J. Phys.: Condens. Matter* **3** 3677