X-ray study of phase transitions in $Cs_3Sb_2I_9$ crystal

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Abstract

An X-ray study of three phase transitions (PTs) at 86, 78 and 72 K has been carried out for the trigonal modification of the $Cs_3Sb_2I_9$ crystal (space group P-3m1, $a = 8.460$ Å, $c = 10.398$ Å). The $T_{c1} = 86$ K PT preserves the trigonal symmetry and is associated with the doubling of the c-parameter. At $T_{c2} = 72$ K a doubling of a and b is observed. An intermediate incommensurate phase with $q_1 = 1/2c^*$, $q_2 = (1/2 - \delta)a^* + 1/2c^*$ has been detected in the temperature range of 78–72 K. The lock-in PT at 72 K has a first order character. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

$Cs_3Sb_2I_9$ belongs to a wide family of compounds with the general formula $A_3B_2X_9$ (A is an alkali metal; B = Sb, Bi, Fe, As, Tl, Cr, W, Mo; X = Cl, Br, I). These compounds have been studied at room temperature and classified according to various structural types [1]. Their structure contains units formed by close-packed layers with Sb atoms occupying octahedral cavities formed by I atoms [2]. Two-thirds of the iodide octahedra are filled by Sb atoms. The SbI_6 octahedra are connected through three vertices with the other three octahedrons. It is the existence of these units that makes the crystal so flacky. The crystal $Cs_3Sb_2I_9$ exhibits different polytypic modifications [2]: the first one crystallizes in the space group P6₃/ mmc [1] whereas the second crystallizes in the space group P-3m1 [2]. Different physical properties and ^{127}I NQR of the trigonal modification were studied over a broad temperature range [3]. The results revealed the existence of the PT at 86 and 72 K. It should be mentioned that the X-ray study of the phase transitions in this compound has been partially stimulated by the finding of the incommensurate phase in the hexagonal $Cs_3Bi_2I_9$ [4].
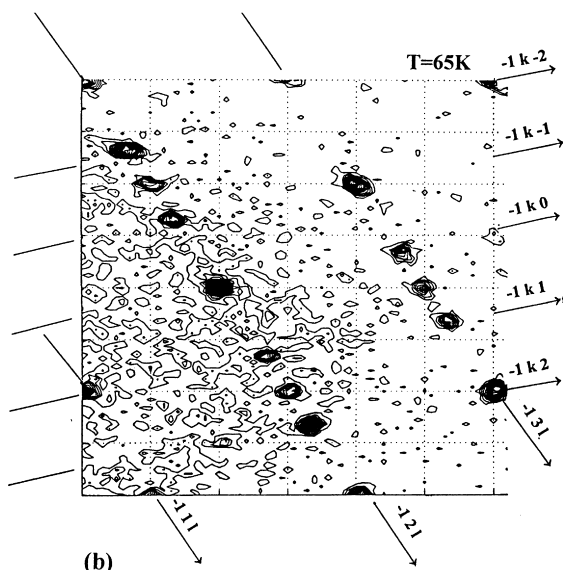
2. Experimental

Single crystals of $Cs_3Sb_2I_9$ were grown using the Bridgman method as described in Ref. [3]. The crystals form fragile plastic plates and have a natural trend for cleavage in the [0 0 1] direction. X-ray studies were performed on a four-circle "Huber" 5042 diffractometer equipped with a low temperature

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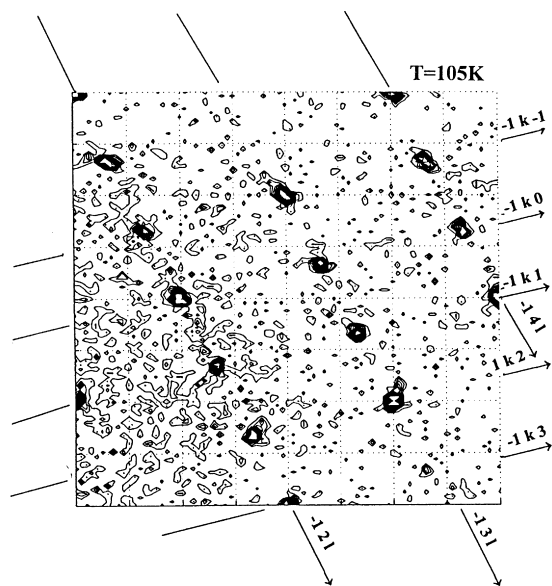
(a)

(b)

Fig. 1. Section of the plane $(-1\ k\ l)$ of the reciprocal space at (a) 105 K and (b) 65 K.

adapter Displex 202 using two cycles of helium extension (with MoKα-radiation and a plumbago monochromator). The accuracy of the temperature stabilization was 0.5 K. The measurements were performed on a small plate (0.4 × 0.4 × 0.07 mm^3) adjusted on a glass stick with wax. Also a two-circle
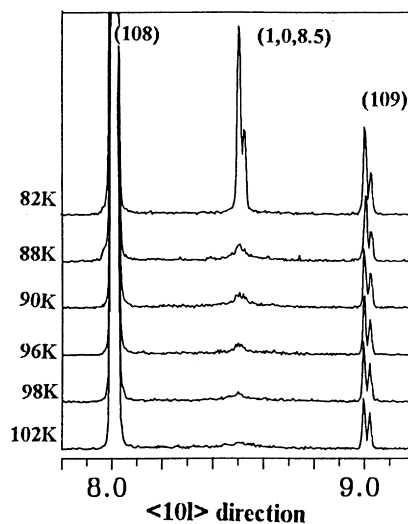

Fig. 2. The formation of the superstructural reflection $(1\ 0\ 8\frac{1}{2})$ from the diffuse spot. The doubling of the peaks is due to the existence of CuKα1 and CuKα2 in the X-ray beam.

"Siemens" D500 diffractometer with CuKα-radiation equipped with helium cryostat was used. The diffractometer is conceived for the study of separate planes in the reciprocal space of specifically oriented monocrystals. The temperature was controlled within 0.1 K over the whole temperature range (273–4 K).

The experiment on the four-circle diffractometer was carried out in the temperature range 273–50 K. The search for satellites was done by q-scans of the reciprocal space. The small samples used for these measurements were unfortunately deformed resulting from chipping off from a bulk crystal. The width of the strain affected reflections was about 4° in ω. Consequently, this caused difficulties in the precise indexing of the weak satellite reflections. The final indexing was performed on the two-circle diffractometer using a large crystalline plate (5 × 8 × 1 mm^3). The measurements were performed in the temperature range of 273–4.2 K for the $(0\ k\ l)$ and $(h\ 0\ l)$ planes. The crystal produced good quality data, which allowed the precise indexing of the weak satellites and measurements of lattice parameters. c was determined from the position of the center of mass of $(0\ 0\ 16)$ reflection measured in the $\theta/2\theta$ mode. The value of a was calculated from the distance between 108 and −108 reflections. The standard deviations are 0.001 and 0.01 E for the c and a parameters
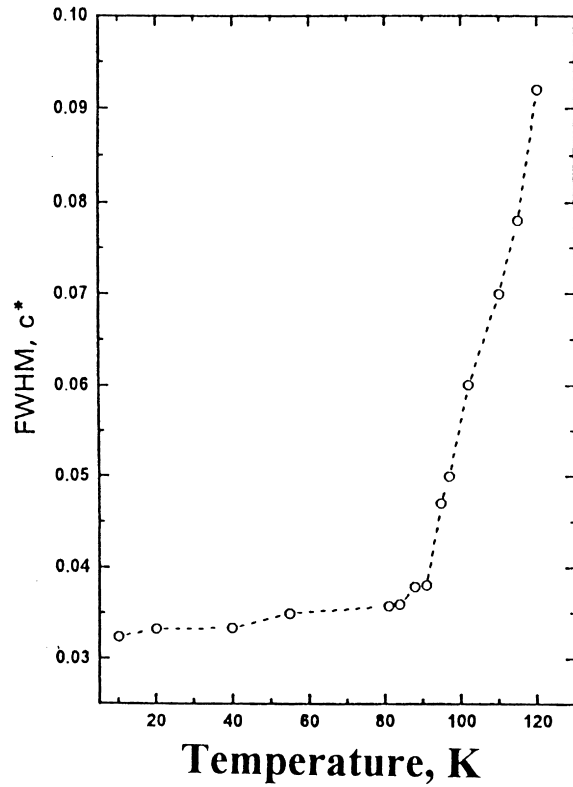
Fig. 3. Full width at half maximum (FWHM) of the superstructural reflection $(1\,0\,8\frac{1}{2})$ versus temperature.
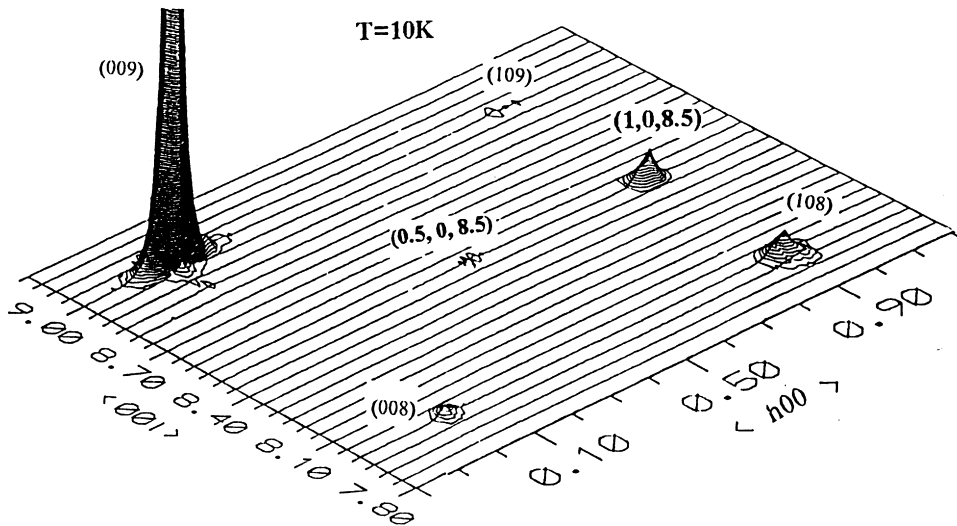

Fig. 4. Section of the plane ($h\,0\,l$) of the reciprocal space at 10 K. Four main reflections and two superstructural peaks $(\frac{1}{2},0,8\frac{1}{2})$ and $(1,0,8\frac{1}{2})$.
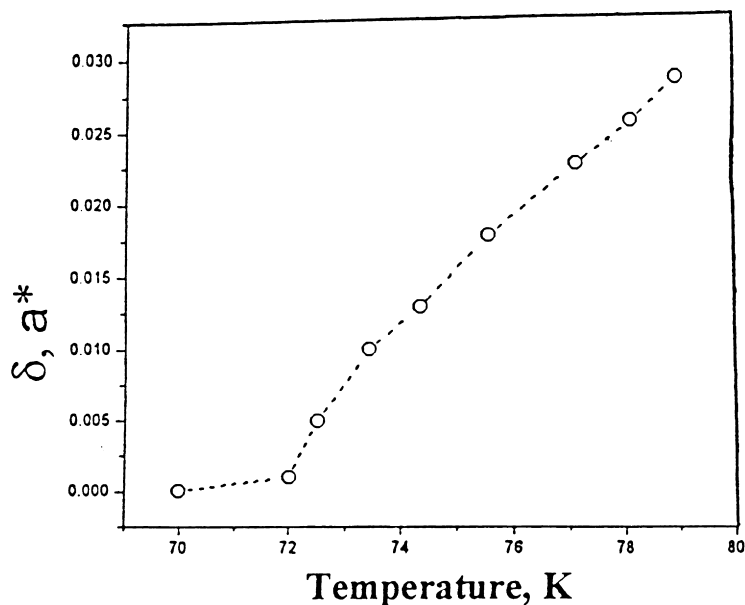
Fig. 5. Misfit parameter δ versus temperature.

respectively. The misfit parameter δ was determined from the position of the satellite reflection $(-1/2 + \delta, 0, 8 + 1/2)$.

3. Results and discussion

Fig. 1 shows a q-scan of the plane $(-1\,k\,l)$ performed on the four-circle diffractometer at 105 and 65 K. The appearance of satellites doubling c-period can be seen. The q-scans are made with the steps $\Delta k = 0.02$, $\Delta l = 0.03$. The search for satellites with mixed components $(h + \Delta h, k + \Delta k, l + \Delta l)$ was unsuccessful. Fig. 2 reveals the appearance of satellites in positions $(h, k, l + 1/2)$. The formation of the superlattice reflections from the diffuse spots starts far above the transition temperature T_{c1}. Fig. 3 gives the width of the satellite versus temperature. The appearance of the superstructural reflections in positions $(h\,k\,l + 1/2)$ can be registered below 86 K. In the new phase with $c' = 2c$, the satellites appear in accordance with the extinction rule $(0\,0\,l,\ l = 2n)$. The PT at 86 K does not change the geometry of the reciprocal space and no indication of twinning is observed in the new phase. According to the X-ray data, it appears that the trigonal symmetry is preserved below 86 K.

Note that the increase of the ^{127}I NQR line number below 86 K is compatible with a doubling of the lattice parameter along c.

Below 78 K new superstructure reflections were observed in positions $(h + 1/2, k, l + 1/2)$. Fig. 4 shows both types of satellites at 10 K. These satellites appear in accordance with the trigonal symmetry. The precise indexing of these satellites showed that in the temperature range (78–73 K) the satellites are incommensurate with a small misfit parameter δ ($h + 1/2 + \delta, k, l + 1/2$). Fig. 5 illustrates the temperature dependence of the misfit parameter δ. At 72 K, δ vanishes. The satellites $(h\,k\,l + 1/2)$ show no temperature dependence. Fig. 6. presents the temperature dependence of the lattice parameters a and c. In the incommensurate phase c is nearly temperature independent and at 72 K it changes discontinuously. That is a direct evidence of a first order PT down to 4.2 K when the parameters change monotonously. The state of the sample depends on its thermal history. The samples did remain in the mono-domain state down to 4.2 K after crossing slowly through the first order PT. The sample transformed to a multi-domain state following a quick crossing through the PT at 72 K. No evidence for any additional PT were found in the temperature interval 4.2–273 K.
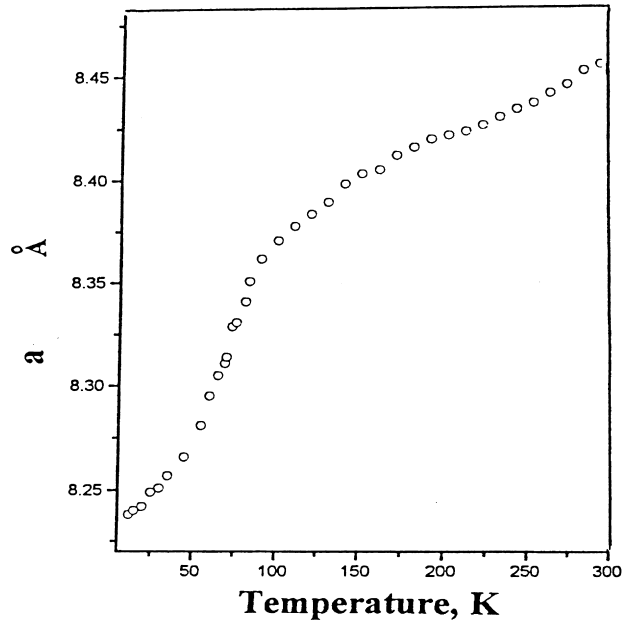
(a)
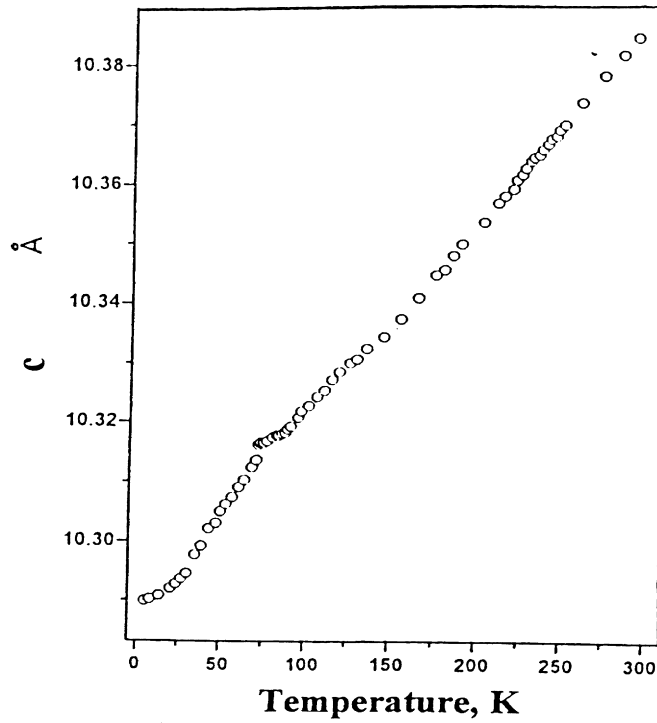
(b)

Fig. 6. Lattice parameters a—(a) and c—(b) versus temperature.

4. Conclusions

The present X-ray study revealed the following sequence of modulated phases in the trigonal modification of $Cs_3Sb_2I_9$, in the temperature range 4.2–273 K:

1. Normal (P-3m1, $Z = 1$): commensurately modulated, trigonal (P3c1 ?), $Z = 2$, $q_1 = 1/2c^*$, $T_{c1} = 86$ K.
2. Commensurately modulated: incommensurate, trigonal, $q_i = 1/2c^* + (1/2 + d)a$; $q_1 = 1/2c^*$, $T_i = 78$ K.
3. Incommensurate: phase (X), it has modulation vector $q_c = 1/2c^* + 1/2a^*$; $q2 = 1/2c^*$ in the geometry of the privies phase, $T_{c2} = 72$ K.

Acknowledgements

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