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Anomalous thermal expansion of silver chlorate in the tetragonal and cubic phases

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Silver chlorate ($AgClO_3$) undergoes a phase transition from a tetragonal to a cubic phase at 139° C. The temperature dependence of lattice parameters and the coefficient of thermal expansion in the tetragonal phase between 23° C and 130° C and in the cubic phase between 140° C and 184° C have been investigated. The lattice parameters in the tetragonal phase and the lattice parameter in the cubic phase increase with temperature. In the tetragonal phase the coefficient of expansion (α_c) increases with temperature whereas the coefficient of expansion along a perpendicular direction (α_a) decreases with increasing temperature. In the cubic phase the coefficient of expansion shows a pronounced decrease with increasing temperature. These results have been discussed in the light of the known structure.

1. Introduction

Silver chlorate crystallizes at room temperature in the space group *I*4/*m* of the tetragonal system [1]. Recent studies on the temperature dependence of the nuclear quadrupole resonance (NQR) spectrum of ^{35}Cl in $AgClO_3$ have shown that it undergoes a first-order phase transition between 140 and 150° C [2–4]. Kasprzak and Pietrzak have also reported that the high-temperature phase is cubic with a lattice constant of 0.942 nm at 162° C [4].

In a recent communication [5] the authors have given an account of their differential scanning calorimetric (DSC) and X-ray diffractometric studies on the temperature and the nature of the phase transition in $AgClO_3$. It was found that an endothermic phase change occurs at 139° C and that the accompanying change of enthalpy is 3.12 cal g^{-1} (0.596 kcal mol^{-1}). It was also established that the crystal transforms to a primitive cubic lattice with a lattice parameter of 0.6679 nm at 140° C. It was further shown that the cubic unit cell contains four molecules of $AgClO_3$. This conclusion was based on the argument that the volume occupied by a single molecule in the cubic cell, although somewhat larger than that in the tetragonal cell, would be of the same order of magnitude, whatever the readjustment involved in the phase transition.

No data are available in the literature on the temperature variation of the lattice parameters and the coefficients of thermal expansion of this crystal. The authors have undertaken a systematic study of this aspect both in the low-temperature tetragonal and the high-temperature cubic phases.

2. Experimental procedure

Silver chlorate powder was prepared by following the procedure outlined by Nicholson *et al.* [6]. The X-ray powder diffractograms of $AgClO_3$ were taken with a Berthold θ–60 diffractometer based on a Bragg–Brentano geometry [7]. Cobalt $K\alpha_1$ radiation obtained using a quartz crystal monochromator was used for taking the traces. The diffractometer had arrangements for heating the sample to any desired temperature, which could be controlled to an accuracy of ± 1° C. The specimen could be maintained under a vacuum of

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the order of 10^{-6} Torr. The specimen was in the form of a platelet of dimensions 25 mm x 20 mm x 2 mm and was obtained by compressing the powder to a pressure of about 8 tons in^{-2} (1.10 x 10^8 NT m^{-2}) Bragg angles from 8° to 67° could be covered in any run.

A full trace, covering the whole angular region, was taken at 23° C, while three more traces were recorded in the tetragonal phase at 62° C, 90° C and 130° C, covering only the high-angle region between 48° and 67°. All the reflections recorded on the trace taken at 23° C could be indexed on the basis of body-centred tetragonal unit cell. The lattice parameters were calculated by Cohen's method [8], using Bragg reflections (316), (640), (505), (633), (642), (800), (660), (822), (644) and (622). The error function $\sin^2 2\theta$, which was employed for an analytical extrapolation, was found to give consistent results. The standard errors in the lattice parameters was estimated by the method of Jette and Foote [9]. The coefficients of expansion at different temperatures were evaluated using the graphical method suggested by Deshpande and Mudholkar [10].

3. Results

3.1. The tetragonal phase

Table I gives the lattice parameters at various temperatures between 23 and 130° C, with the values of the axial ratio (*c/a*) and the volume of the unit cell per molecule. The errors in the *a* and *c* parameters are found to be ± 0.0002 nm and ± 0.0004 nm respectively. From these data the temperature variations of the two principal coefficients of thermal expansion (α_a and α_c) were evaluated. The coefficients could be represented by the following relations:

$$\alpha_a = 53.69 \times 10^{-6} - 51.34 \times 10^{-8} T + 15.75 \times 10^{-10} T^2$$

$$\alpha_c = 30.32 \times 10^{-6} + 43.78 \times 10^{-8} T + 23.48 \times 10^{-10} T^2$$

where *T* is the temperature in degrees Celcius. The temperature variation of α_a and α_c in the tetragonal phase are shown in Fig. 1.

TABLE I Lattice parameters of $AgClO_3$ at different temperatures in the tetragonal phase

T (° C)	*a* (nm)	*c* (nm)	*c/a*	Volume/molecule (nm^3)
23	0.8492	0.7919	0.932	0.071 38
62	0.8503	0.7938	0.933	0.071 75
90	0.8509	0.7950	0.934	0.071 96
130	0.8515	0.7986	0.938	0.072 38

3.2. The cubic phase

The sample was heated to 140° C for about 12 h and a full trace was recorded. The trace clearly indicated that the transformation was complete as no peak of the tetragonal phase was observed. From a detailed consideration of the allowed and absent reflections [5] it was established that the high temperature form is primitive cubic and not a body-centred cubic as inferred from the results of Kasprzak and Pietrzak [4]. The reflections (510), (511), (520), (521), (522), (531), (600), (532), (621), (541), (533) and (630), recorded in the Bragg-angle region 43° to 67°, were used to evaluate the lattice parameters in the cubic phase.

Table II gives the values of the lattice parameters at different temperatures. The standard error in the lattice parameter is ± 0.0001 nm. The values of

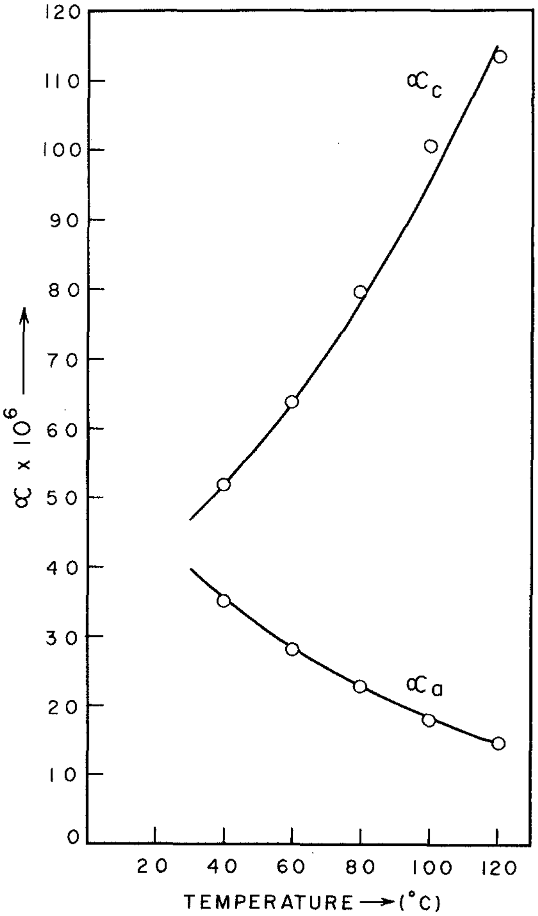

Figure 1 Temperature variation of α_a and α_c in the tetragonal phase of $AgClO_3$.

TABLE II Lattice parameters of $AgClO_3$ at different temperatures in the cubic phase

T (°C)	a (nm)	Volume/molecule (nm^3) calculated on the assumption of 4 molecules/unit cell
140	0.667 95	0.074 50
145	0.668 14	0.074 56
159	0.668 51	0.074 68
184	0.668 79	0.074 78

volume per molecule calculated on the assumption of 4 molecules/unit cell are also given in the same table. The value of the coefficient of thermal expansion was evaluated from a temperature parameter plot employing the method suggested by Deshpande and Mudholkar [10].

The following expression represents the variation of α with temperature:

$$\alpha = 59.46 \times 10^{-6} - 20.18 \times 10^{-7}(T - 140) + 2.09 \times 10^{-8}(T - 140)^2$$

where T is temperature in degrees Celcius. The temperature variation of α in the cubic phase is shown in Fig. 2. The error in the values of the coefficients of expansion are about 5%.

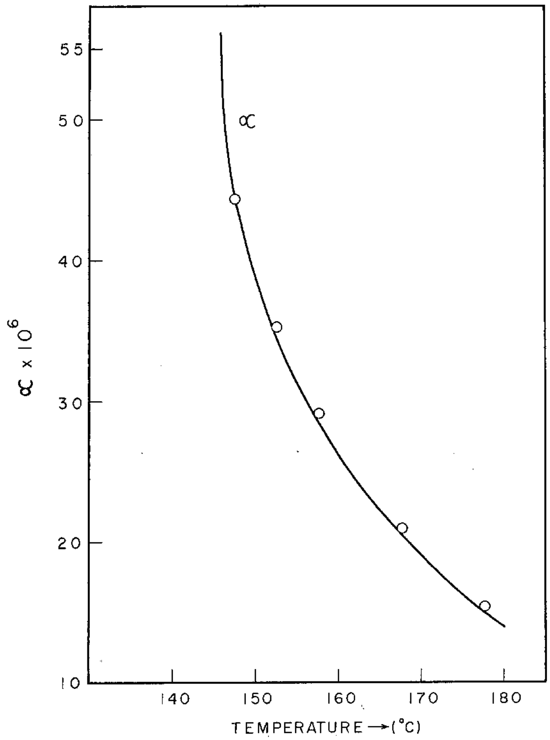

Figure 2 Temperature variation of α in the cubic phase of $AgClO_3$.

4. Discussion

The main features of the data given above can be summarized as follows.

(a) Both the lattice parameters of the tetragonal cell increase with temperature.

(b) The coefficients of thermal expansion along the tetragonal axis (α_c) increases with temperature whereas the coefficient in a perpendicular direction (α_a) decreases with increasing temperature.

(c) The axial ratio (c/a) increases from 0.932 at 23° C to 0.938 at 130° C.

(d) The volume of the tetragonal cell per molecule increases with temperature. The average coefficient of expansion in the tetragonal phase between 23 and 130° C is $140.55 \times 10^{-6}/°C$.

(e) Although in the cubic phase the lattice parameter increases with temperature the coefficient of expansion shows a pronounced decrease with increasing temperature. The mean coefficient of expansion between 140 and 184° C is $83.62 \times 10^{-6}/°C$.

(f) In the cubic phase, the volume of the unit cell per molecule increases with temperature.

(g) From an evaluation of the data on volume/molecule as a function of temperature it is confirmed that $AgClO_3$ undergoes a first-order phase transition as observed by Ivanov *et al.* [3]. A plot of temperature versus volume per molecule is shown in Fig. 3.

These features are, in general, in accordance with the normal thermal expansion behaviour of a crystal except for two observations which

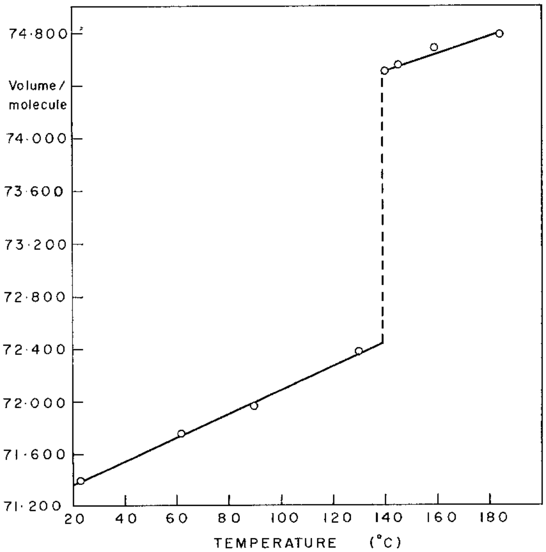

Figure 3 A plot of temperature against volume/molecule in the tetragonal and cubic phases of $AgClO_3$.

deserve special mention. One of these is the decrease in (α_a) in the tetragonal phase as against an increase in (α_c). The other is the pronounced fall in the value of the coefficient of thermal expansion in the cubic phase with rising temperature. An attempt is made here to suggest probable reasons for these pecularities.

The value of the axial ratio (c/a) in the tetragonal phase is less than unity at room temperature and increases with temperature. However, its increase with the rise of temperature is suggestive of a tendency to approach the value of unity, true for a more symmetric cubic structure. Further the overall weakening of the bonds in the crystal structure with the rise of temperature and consequent thermal expansion should invariably result in an increasing trend in the values of the coefficients of expansion. Any observation contrary to this suggests that some progressive structural changes may be occurring in the crystal which when superposed over the general thermal expansion might result in the observed decrease in the coefficient of expansion with rising temperature. Such an anomalous behaviour in the thermal expansion behaviour of ammonium dihydrogen phosphate has been observed and explained by Deshpande and Khan [11].

Progressive structural changes responsible for the peculiarity of thermal expansion in $AgClO_3$ might arise due to a distortion of the chlorate ion from the trigonal symmetry which it assumes in crystals of sodium chlorate and potassium chlorate. Hence a comparison of the structure of $AgClO_3$ with other monovalent chlorates such as $NaClO_3$ and $KClO_3$ would be of some interest. Recent structural studies on $NaClO_3$, reported by Burke-Laing and Trueblood [12] have shown that all the three Cl–O bond lengths are 0.1502 nm and all the three O–Cl–O angles are 106.8°. In $KClO_3$, studied by Bats [13], two of the Cl–O bond distances are 0.14736 nm and the third is 0.14789 nm, while two of the three O–Cl–O angles are 106.47° and the third is 106.78°. It is thus found that the chlorate ion has the full regular trigonal symmetry in sodium chlorate and is only slightly distored in potassium chlorate.

The only data on the structure of $AgClO_3$ are those by Na'ray-Szabo' and Poc'za [1]. According to this report two of the Cl–O bonds are 0.145 nm and the third is 0.144 nm, while two of the O–Cl–O angles are 110.52° and the third is 112.0°. These values, particularly those of the angles, are very much different from the values in $NaClO_3$ and $KClO_3$ crystals. Although the data on $AgClO_3$ are old and call for a revision, it can be said that there exists, in this crystal, a large degree of distortion in the configuration of the ClO_3 ions, particularly in the values of the angles. These distortions are certainly the result of the adjustment of a basically trigonal structure into a tetragonal unit cell. The weakening of the bonds with a rise in temperature of the crystal offers an opportunity to the strained ClO_3 ions to get rid of the distortions and progressively try to approach a more symmetric configuration. It may also be said that these progressive changes in the structural parameters might finally culminate in the phase transition from a tetragonal to a cubic lattice.

The pecularity in the temperature dependence of the coefficient of expansion in the cubic phase, may be due to some further readjustments of the structural parameters. This view is supported by a study of the DSC trace shown in Fig. 4. The large and sharp endothermic peak in this trace beginning at 139° C is due to the first-order phase transition discussed by Desphande *et al.* [5]. The trace shows another smaller and broader peak in the high

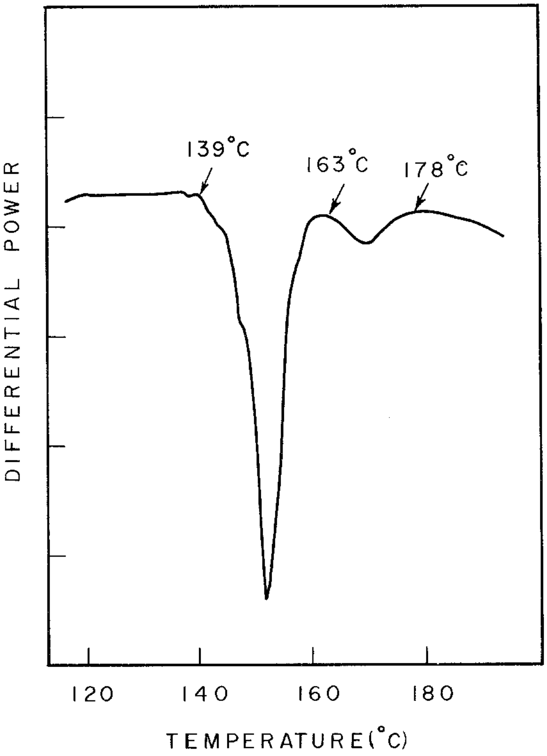

Figure 4 DSC trace of $AgClO_3$.

temperature region. The exact origin of this has not been investigated. It may, however, be said to indicate some process of adjustment of structural parameters occurring in the lattice and may be responsible for the pecularities observed in the thermal expansion behaviour. Work on the refinement of the structure at room temperature and structure determination of the high-temperature phase is in progress in this laboratory.

5. Conclusions

Silver chlorate undergoes a first-order phase transformation from tetragonal to cubic phase at 139° C. A detailed study of temperature variation of lattice parameters and thermal expansion of $AgClO_3$ in the tetragonal and cubic phases indicates that in the tetragonal phase α_c increases and α_a decreases with increasing temperature. In the cubic phase, also, α decreases with increasing temperature. The anomalous behaviour of the observed coefficients of expansion in $AgClO_3$ are explained on the assumption that the lattice is under some constraints in the tetragonal phase.

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References

1. I. NA'RAY-SZABO' and J. POC'ZA, *Z. Krist.* **104** (1942) 28.
2. S. K. SHCHERBAKOVA, A. A. BOGUSLAVSKII, V. M. BURBELO and R. Sh. LOTFULLIN, *Izv. Akad. Nauk, SSSR, Ser. Fiz.* 39 (1975) 2505.
3. I. P. IVANOV, A. A. BOGUSLAVSKII, R. Sh. LOFFULLIN and A. P. ZENKOV, *ibid.* 39 (1975) 2513.
4. J. KASPRZAK and J. PIETRZAK, *Phys. Stat. Solidi (a)* 55 (1979) K115.
5. V. DESHPANDE, S. V. SURYANARAYANA and C. FRANTZ, *Bull. Mater. Sci. (India)*, in press.
6. D. G. NICHOLSON and C. E. HOLLEY, in "Inorganic Synthesis", Vol. 2, Edited by W. Conard Fernelius (McGraw-Hill, New York, 1946) p. 4.
7. C. FRANTZ, PhD University of Nancy, France (1970).
8. M. U. COHEN, *Rev. Sci. Instrum.* 6 (1935) 68.
9. E. R. JETTE and F. FOOTE, *J. Chem. Phys.* 3 (1935) 605.
10. V. T. DESHPANDE and V. M. MUDHOLKAR, *Acta Crystallogr.* 13 (1960) 483.
11. V. T. DESHPANDE and A. A. KHAN, *ibid.* 16 (1963) 936.
12. M. E. BURKE-LAING and K. N. TRUEBLOOD, *ibid* B33 (1977) 2698.
13. J. W. BATS, *ibid* B34 (1978) 1679.

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