A back-reflection x-ray camera for thermal-expansion studies and the thermal expansion of NaCl from —180°C to 200°C

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With 3 figures

Auszug

Es wird eine Rückstrahl-Kammer auf Aufnahmen zwischen —180°C und 200°C beschrieben, die auf die Länge des Präparats keinen Temperaturgradienten aufweist und bis auf ± 0,5°C konstant ist.

Mittels der Kammer wurde die Wärmeausdehnung von aus Schmelzflüssen gezogenen NaCl-Kristallen im oben angegebenen Bereich gemessen. Die Ergebnisse sind im Einklang mit der Wärmeausdehnung, gemessen von R. Srinivasan (an Kristallen der gleichen Züchtung) und von anderen Autoren nach der üblichen Methode. Die Übereinstimmung läßt vermuten, daß Gitter-Fehlstellen in NaCl-Kristallen bei Zimmertemperatur, wenn überhaupt vorhanden, gleichmäßig verteilt sein müssen.

Abstract

This paper describes a simple back-reflection x-ray camera for thermal studies from —180°C to 200°C. This is a modification of the Unicam single-crystal goniometer S 25. The camera effectively eliminates any temperature gradient along the length of the specimen and the temperature can be maintained constant to ± 0.5°C. The deposition of ice on the specimen at low temperatures is also successfully prevented. Using this camera the lattice thermal expansion of melt-grown single crystals of NaCl was measured over the range —180° to 200°C. These results are in very good agreement with the macroscopic thermal expansion of the same batch of crystals made by Dr. R. Srinivasan, as also those obtained by other authors for this substance. This agreement suggests that if lattice defects are present in NaCl at room temperature they must be uniformly distributed throughout the volume of the crystal.

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Introduction

After the classical experiments of FIZEAU[1] on the measurement of the thermal expansion of NaCl by interferometric techniques many investigators have interested themselves in the thermal expansion of this substance. At present fairly accurate values of the macroscopic thermal expansion coefficients of NaCl exist from $-180\,°C$ to $400\,°C$. On the other hand the x-ray data for lattice thermal expansion coefficients of NaCl are not so satisfactory. There are no systematic measurements available at low temperatures and the data at elevated temperatures are somewhat contradictory. For example the lattice-expansion values of NaCl reported by SAINI[2] are much greater than the corresponding macroscopic values, while those of BASU and MAITRA[3] (for rocksalt) are definitely lower. Further GOTT[4] has reported that the x-ray coefficients are consistently lower than the macroscopic coefficients in the case of KI, KBr and LiF, the discrepancies being sometimes as high as 15 to $20\,°/_0$. This was contradicted by the experiments of CONNELL and MARTIN[5]. Accurate measurements of the lattice-expansion coefficients are therefore necessary to resolve this controversy.

STRAUMAINS[6] has recently established that NaCl crystals contain about 10^{18} frozen-in vacancies per cm^3 even at ordinary temperatures and that this concentration is independent of annealing. It is of importance to determine whether this large concentration of defects influences the macroscopic and lattice expansions in a similar manner. Consequently the accurate determination of the x-ray lattice-expansion coefficients was undertaken by the present writers using the same batch of crystals of NaCl with which

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[1] H. FIZEAU, Mémoire sur la dilatation des corps solides par la chaleur. C. Rend. Acad. Sci. [Paris] 62 (1866) 1133—1148; also 64 (1867) 314—323.

[2] H. SAINI, Dilatation thermique du sel gemme et du NaCl pur. Helv. Physica Acta 7 (1934) 494—500.

[3] S. BASU and A. T. MAITRA, Thermal coefficient of rocksalt by x-ray reflection. Ind. J. Physics 12 (1938) 305—316.

[4] A. GOTT, Thermische Gitterdehnung und makroskopische Ausdehnung von Alkalihalogenidschmelzflußkristallen. Ann. Physik 41 (1942) 520—536.

[5] L. F. CONNELL and H. C. MARTIN, Concerning reported discrepancies between x-ray and macroscopic measurements of thermal expansion of some alkali halides. Acta Crystallogr. 4 (1951) 75—76.

[6] M. E. STRAUMANIS, Density determinations by a modified suspension method; x-ray molecular weight, and the soundness of sodium chloride. Amer. Mineralog. 38 (1953) 662—670.

SRINIVASAN[7] obtained precise data on the macroscopic thermal-expansion coefficients.

Preliminary experiments showed that the errors in x-ray measurements were mainly due to the *actual temperature* of the experimental crystal not being measured accurately and this determination was sometimes made more difficult by the presence of a marked temperature gradient along the length of the specimen. In back-reflection techniques, when temperature differences of less than 20 °C to 25 °C are used, the reflection of the $CuK\alpha_1$ radiation at one temperature tends to overlap with the reflection of the $K\alpha_2$ radiation at a neighbouring temperature. This also introduces inaccuracies in measurement. A fairly satisfactory camera in which these difficulties have been eliminated has been constructed and using this camera the thermal expansion of NaCl has been studied from —180° to 200 °C.

The constant-temperature arrangement

Figure 1 gives the arrangement[8] fixed on the conventional goniometer head used for maintaining the crystal at any steady temperature between —180 °C and 200 °C. For the low-temperature investiga-
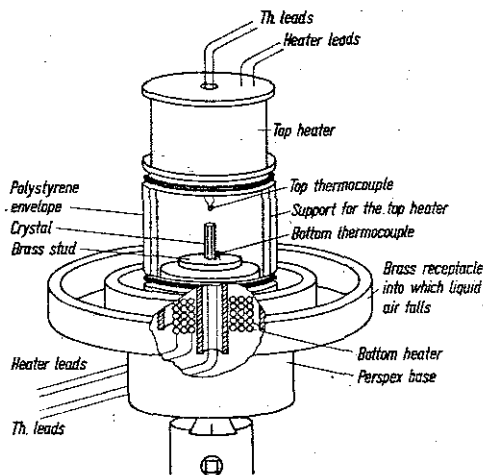

Fig. 1. The constant-temperature arrangement that is mounted on the goniometer head

[7] R. SRINIVASAN, Thermal expansion of sodium and potassium chlorides from liquid air temperatures to + 300 °C. J. Ind. Inst. Sci. 37 (1955) 232—241.

[8] M. A. VISWAMITRA, Ph. D. Thesis, Indian Institute of Science (1959); see also Proc. Ind. Acad. Sci. 49 (1959) 326—332.

tions the LONSDALE and SMITH[9] method of cooling was adopted. Liquid air, filtered of its solidified impurities, is allowed to flow through a thin stainless-steel hypodermic needle fixed at the lower end of a Lonsdale flask. The stream of liquid air falls on a circular brass plate with grooves in it. The crystal is fixed to a central brass stud and it is cooled by conduction. A perspex block insulates the goniometer from the cold plate, perspex being chosen as it showed negligible warping at low temperatures. By passing currents through two heaters, one above and the other below the crystal, the specimen can be maintained at any desired temperature from $-180°$ to room temperature. When the flow of liquid air is stopped the crystal can be heated to $+200°C$. The lower heater bobbin is imbedded in the perspex block while the upper one is supported on the brass plate by two slender brass legs. The space between the two heaters serves as the crystal chamber and it is isolated from the outside by a strip of polystyrene. This helps to eliminate fluctuations in the specimen temperature due to air currents and it also effectively prevents deposition of ice on the crystal during low temperature work. Two calibrated iron-constantan thermocouples measure the temperatures at the base and top of the crystal. The leads to the thermocouple and heaters are taken out through tight fitting holes drilled in the perspex blocks. If this was not done these leads usually snapped shortly after commencing the oscillation.

To maintain the top and bottom thermocouples at exactly the same temperature it was necessary to pass different currents (controlled by two independent autotransformers) through the two heaters. In the early stages of experimentation a third thermocouple was used to explore the temperature gradients in the crystal chamber. The differences in temperature along the length of the specimen was usually less than $0.5°C$ in the range of temperatures used and could if necessary be corrected for as it was reproducible. The temperature itself could be maintained constant to $\pm 0.5°C$ and could be measured to $\pm 0.2°C$.

The deposition of ice during the experiments at low temperatures was completely prevented by a very thin bag of polythene, one end of which was tied at the goniometer end and the other end to the bottom of the Lonsdale flask. The slight excess of pressure inside caused by the evaporating liquid air prevents moist air from diffusing inside.

[9] K. LONSDALE and H. SMITH, Crystal structure of cyclohexane at $-180°C$. Phil. Mag. 28 (1939) 614—616; see also J. Sci. Instr. 18 (1941) 133—135.

The back-reflection camera

The goniometer with the crystal chamber attached was mounted on the spindle of a Unicam single-crystal x-ray goniometer (S 35). The heater and thermocouple leads were taken out through a hole made in the base plate. The back-reflection cassette supplied by the manufacturers was not used because of the small specimen-to-film distance. Instead, a new back-reflection arrangement, illustrated in
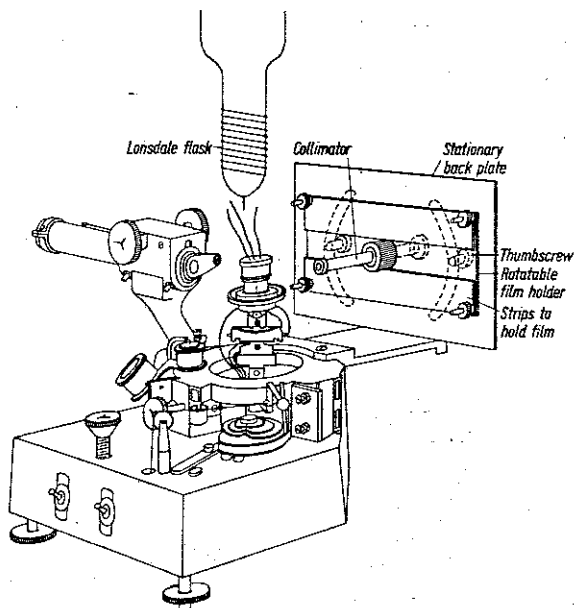

Fig. 2. The back-reflection camera for thermal expansion studies

Fig. 2, was screwed on so that the specimen-to-film distance was nearly 14.5 cm. The only satisfactory method of separating the overlapping $K\alpha_1$ and $K\alpha_2$ reflection at two neighbouring temperatures would be to move the film after each exposure. Instead of using the arrangement due to UBBELOHDE[10] it was decided to use the simpler procedure of rotating the film holder through a small angle about the axis of the collimator after each exposure.

The back-reflection camera consists of a stationary back plate at the centre of which a collimator can be inserted through a cylindrical

[10] A. R. UBBELOHDE, A multiple exposure x-ray spectrometer. J. Sci. Instr. 16 (1939) 155—161; see also Proc. Roy. Soc. [London] 181 (1943) 415—427.

bearing, and fixed in any position required by the focussing condition[11]. The film holder is another flat plate capable of being rotated about the collimator bearing. It can be fixed at any orientation by two thumb screws provided behind the back plate. The film holder can be mounted or removed without disturbing the collimator. The x-ray film enclosed in a black paper is punched centrally and is held in the film holder by two brass strips fixed by four thumb screws. The film holder is held flush against the back plate but it may be fixed at any desired orientation by two thumb screws at the back. A central nut prevents any light leakage through the punched hole. Screws and studs are provided to make fine adjustments of the cassette.

Experimental procedure

The specimen to film distance was accurately determined using 99.99 % pure aluminium powder ($d_{100}^{25} = 4.0493$ Å) as the standard[12]. The crystals studied in the present investigation were cut from a big crystal grown in the laboratory from the melt by the Kyropoulos technique. 'Analar' grade of chemicals were used. Each specimen was ground to a cylinder (2.5 mm height and 0.2 mm diameter) with its axis parallel to the cubic axis of the crystal. It was annealed at 400 °C for a few hours, sealed into a thin-walled glass capillary and mounted on the central brass stud of the crystal chamber with silico-phosphate dental cement. The cement was allowed to set for two hours and then subjected to alternate heating and cooling to avoid any possible misalignment during the experiments. The crystal was centered and aligned, first optically, and then accurately by taking a few oscillation photographs.

For the exact determination of the spacing it was essential to record a reflection symmetrically on either side of the collimator as this eliminates many errors in measurements. Preliminary experiments showed that the 640 reflection of NaCl was ideally suited for thermal-expansion work with $CuK\alpha$ radiations. The crystal was set to oscillate over a 15° range so that this reflection was recorded on either side of the collimator. Photographs at six successive temperatures were recorded on the same film, the film holder being rotated through

[11] H. S. PEISER, H. P. ROOKSBY and A. J. C. WILSON, X-ray diffraction by polycrystalline materials. Institute of Physics (1955), London, p. 176.

[12] A. IEVINŠ und M. STRAUMANIS, Die Gitterkonstante des reinsten Aluminiums. Z. physik. Chem. B 34 (1936) 402—403.

a small angle after each exposure. Two independent sets of photographs were taken for each temperature range, one when the crystal was being heated and the other when it was cooled. A second specimen was also investigated in a similar manner.

The actual distance on the film between the reflections on either side of the central hole (recorded at any specific temperature) could be measured to an accuracy of ± 0.1 mm and from the knowledge of the film-to-specimen distance (determined to 0.3% accuracy) the spacing of the planes at that temperature could be computed. It is estimated that the spacings are accurate to 0.02%. The lattice thermal-expansion coefficient is calculated from the formula

$$\alpha_t = \frac{d_{t_2} - d_{t_1}}{d_{t_1}(t_2 - t_1)}$$

where t_2 and t_1 are two neighbouring temperatures, d_{t_2} and d_{t_1} are the corresponding lattice spacings, and t is the mean of t_1 and t_2. Measurements have been made for every $25\,°C$ from $-160\,°C$ to $+200\,°C$ while the specimen was being heated and cooled.

Results

The curve of the lattice-expansion coefficient of NaCl against temperature is given in Fig. 3. The experimental points are marked on it and nowhere does the curve deviate by more than $\pm 1\%$ from the experimental values. Table 1 compares the present lattice values
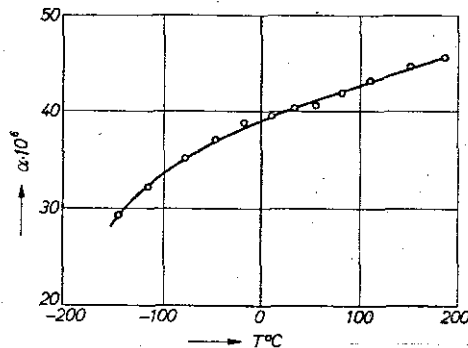

Fig. 3. The variation of the lattice thermal-expansion coefficient of NaCl with temperature

Table 1. *Comparison of the lattice and macroscopic expansion coefficients* $\alpha \times 10^6$

Temperature °C	BUFFINGTON and LATIMER [14]	SRINIVASAN [7]	Present values	Author	Temperature °C	$\alpha \times 10^6$	Present values
−133.0	30.9	29.7	30.5	FIZEAU [1]	40.0	40.4	40.6
−109.8	33.2	33.8	32.7	HENGLEIN [13]	−184/−79	31.0	30.6
−88.0	34.7	35.1	34.4		−79/0	36.7	37.3
−46.5	36.8	36.8	36.8	EUCKEN and DANNOHL [15]	0	40.3	39.1
−9.3	38.5	39.6	38.7		100	41.3	42.8
13.9	39.3	40.2	39.5		200	43.6	46.5
42.0		40.3	40.5		300	47.2	
80.0		41.3	41.8	WALTER et al. [16]	0	39.0	39.1
117.0		43.4	43.2		100	41.9	42.8
152.0		44.7	44.3		300	47.2	
183.0		46.6	45.4				
248.0		49.5					
277.0		50.6					

with the macroscopic values of SRINIVASAN[7] obtained on the same
batch of crystals as well as those of other authors[1,13-16].

Table 2 compares the present lattice values with the lattice values
of various authors[2,3,17-20]. The values entered in the tables have been
read off from Fig. 3. It is estimated that each individual experimental
value is correct to $\pm 3\%$ but the values read from the graph may be
correct to better than $\pm 2\%$.

Table 2.

Comparative study of the lattice-expansion coefficients obtained by various authors

Author	Specimen	Temperature °C	$\alpha \times 10^6$	Present values $\alpha \times 10^6$
LINDEMANN[17]	Rocksalt	50	40.9	41.0
GEISS[18]	Rocksalt	0— 50	40.0	40.0
JAMES[19]	Rocksalt	0—500	38.3	—
BASU and MAITRA[3]	Rocksalt	150	41.41	44.3
		200	41.32	46.1*
SAINI[2]	NaCl	0	35.5	39.1
		50	40.0	41.0
		100	44.4	42.8
		140	48.0	44.3
		140—220	47.0	45.8
STRAUMANIS and IEVINŞ	NaCl	18— 67	40.5	40.7

* extrapolated.

[13] F. A. HENGLEIN, Die thermische Ausdehnung einiger Alkalimetallhalogenide bei tiefen Temperaturen. Z. physik. Chem. 115 (1925) 91—120.

[14] R. M. BUFFINGTON and W. M. LATIMER, The measurement of coefficients of expansion at low temperatures. J. Amer. Chem. Soc. 48 (1926) 2305—2319.

[15] A. EUCKEN und W. DANNOHL, Die thermische Ausdehnung einiger Alkalihalogenide und Metalle bei hohen Temperaturen. Z. Elektrochem. 40 (1934) 814—821.

[16] A. K. WALTHER, W. PH. HASCHKOWSKY und STRELKOW, Die Wärmekonstanten bei hohen Temperaturen: Die Wärmeausdehnung von Steinsalz. Physik. Z. Sowjetunion 12 (1937) 35.

[17] C. L. LINDEMANN, Über die Temperaturabhängigkeit des thermischen Ausdehnungskoeffizienten. Physik. Z. 13 (1912) 737—739.

[18] W. GEISS, Dichtebestimmungen an Steinsalzkristallen. Ann. Physik 76 (1925) 403—408.

[19] R. W. JAMES, The influence of temperature on the intensity of reflexion of x-rays from rocksalt. Phil. Mag. 49 (1935) 585—602.

[20] M. E. STRAUMANIS und A. IEVINŞ, Die Gitterkonstanten des NaCl und des Steinsalzes. Z. Physik 102 (1936) 353—359.

Discussion of results

The (100) spacing of NaCl at 18 °C given by Siegbahn [21] is 5.63936 Å. This spacing at 26 °C would be 5.64112 Å. The value of $d_{100}^{26°}$ computed from the present value is 5.64092 Å. The good agreement indicates the order of accuracy attained in the measurement of lattice spacings in the present experiments. It is also gratifying to note that the lattice-expansion coefficients at 18/67 °C obtained in precision experiments of Straumanis and Ievins [20] (Table 2) agrees to within 0.5% with the present values.

The present x-ray values are in very good agreement with the macroscopic measurements of Srinivasan [7] as also with those of Fizeau [1], Henglein [13], Buffington and Latimer [14]. The values of Eucken and Dannohl [15] are at considerable variance with the present values at higher temperatures. But it may be noted the values reported by these authors are consistently lower than those obtained by other investigators. The lattice-expansion coefficients of naturally occurring rocksalt obtained by Lindemann [17] and Geiss [18] agree very well with the present measurements on pure NaCl. It may be mentioned that Srinivasan also found that the macroscopic expansion coefficients of rocksalt and pure NaCl were practically identical. The values of Basu and Maitra [3] are rather low. Contrary to all other experimenters the values obtained by these authors decrease with increasing temperature. However a study of Table 1 very cleary establishes that the thermal-expansion coefficients of NaCl obtained by x-ray methods and macroscopic techniques in the temperature range —180 °C to + 200 °C are practically identical.

The discrepancies previously observed in the alkali halides were attributed to the existence of Schottky defects. The influence of these defects on the thermal expansion of crystals have been theoretically examined by Miller and Russel [22] and Eshelby [23]. They have shown that the fractional changes in the lattice constants of an alkali halide crystal containing a uniform distribution of point defects would be

[21] M. Siegbahn, The spectroscopy of x-rays, p. 19. Oxford University Press, London, 1925.

[22] H. Miller and B. R. Russel, Effect on distribution of lattice defects within crystals of linear expansion and x-ray lattice constant. J. Appl. Physics 24 (1953) 1248—1249.

[23] J. D. Eshelby, Geometrical and apparent x-ray expansion of a crystal containing lattice defects. J. Appl. Physics 24 (1953) 1249; See also Solid State Physics, Vol. III, (Editor Seitz and Turnbull), Academic Press Inc., p. 114.

exactly what one would infer from the relative changes of the macroscopic dimensions of the crystal. The lattice and expansions would be different if the crystal contains a non-uniform distribution of defects.

The close agreement between the lattice and macroscopic expansions may be interpreted to mean that the number of defects in the crystals is small. But if we accept the findings of STRAUMANIS that there are approximately 10^{18} lattice vacancies per cm^3 in NaCl even at ordinary temperatures, then one must conclude that these defects are uniformly distributed throughout the volume of the crystal in the range of temperatures studied.

It must finally be pointed out that even near the melting point where one may expect a large concentration of SCHOTTKY defects FISCHMEISTER [24] finds that the x-ray lattice expansion is not significantly different from the macroscopic expansion.

Acknowledgement

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[24] H. F. FISCHMEISTER, The thermal expansion of sodium chloride and some other alkali halides at high temperature. Acta Crystallogr. 9 (1956) 416—420.