ment la part due à l'agitation thermique. Il a été possible de déterminer *quantitativement* l'action de l'extinction primaire et le degré de perfection du cristal (taille maximum des blocs de la mosaïque: 0,45μ); il resterait à voir le rôle de l'extinction secondaire, qui est moins important.

Les principales difficultés théoriques ont été rencontrées dans la recherche d'une approximation du spectre des fréquences. Le calcul de la chaleur spécifique, grandeur peu sensible à des variations du spectre des fréquences, a donné des résultats en bon accord avec l'expérience, mais n'a pas permis de faire un choix entre les deux approximations essayées. Les résultats obtenus pour le facteur de température ne concordent pas et la comparaison avec les résultats expérimentaux montre que c'est une répartition identique à celle de l'axe [111] qui est la plus proche de la véritable répartition, mais on peut penser que le calcul complet du spectre des fréquences en résolvant l'équation séculaire pour un grand nombre de points permettrait de diminuer encore l'écart entre les intensités calculées et mesurées. Néanmoins il est vraisemblable qu'il restera toujours un certain écart, en effet les intensités théoriques ont été évaluées à partir des facteurs atomiques de Hartree qui ont été calculés en supposant une symétrie sphérique de la répartition de la densité électronique autour des noyaux, ce qui est certainement inexact. On peut donc penser qu'il serait possible de déterminer à partir de cet écart résiduel la répartition de la densité électronique dans la blende.

Ce travail a été effectué au Laboratoire de Minéralogie et de Cristallographie de la Faculté des Sciences de Paris sous la direction de Monsieur H. Curien.

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The Thermal Expansion of Sodium Chloride and Some Other Alkali Halides at High Temperatures

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X-ray measurements of the thermal expansion of NaCl up to the melting point are reported. Within experimental error, the expansion of the lattice agrees with the macroscopic dilatation, and it is shown that the number of lattice defects present at the melting point cannot be expected to cause a positively detectable difference between them.

The observed non-linearity of the thermal expansion of the alkali halides is shown to be in accord with established lattice-dynamical theory and not to be caused by lattice defects.

Introduction

As a preliminary to cell-constant measurements of the high-temperature modifications of the alkali sulfates (Fischmeister & Lindqvist, 1954) and the alkali nitrates (Fischmeister, 1956), a number of calibration runs with NaCl were made to determine the eccentricity error of the camera as a function of temperature. The apparatus employed was designed for survey rather than for precision work. However, since no X-ray measurements of the high-temperature thermal expansion of sodium chloride seem to have been published, the data derived from these runs are reported below.

Such measurements appeared desirable also from a theoretical point of view because of the suspected contribution of lattice defects to the thermal expansion, to which certain reported discrepancies between dilatometric and X-ray measurements have been ascribed (for a recent review of the literature, see Jost, 1952). For KBr and KI, Connell & Martin (1951) showed that no measurable contribution of lattice defects could be ascertained in the temperature range

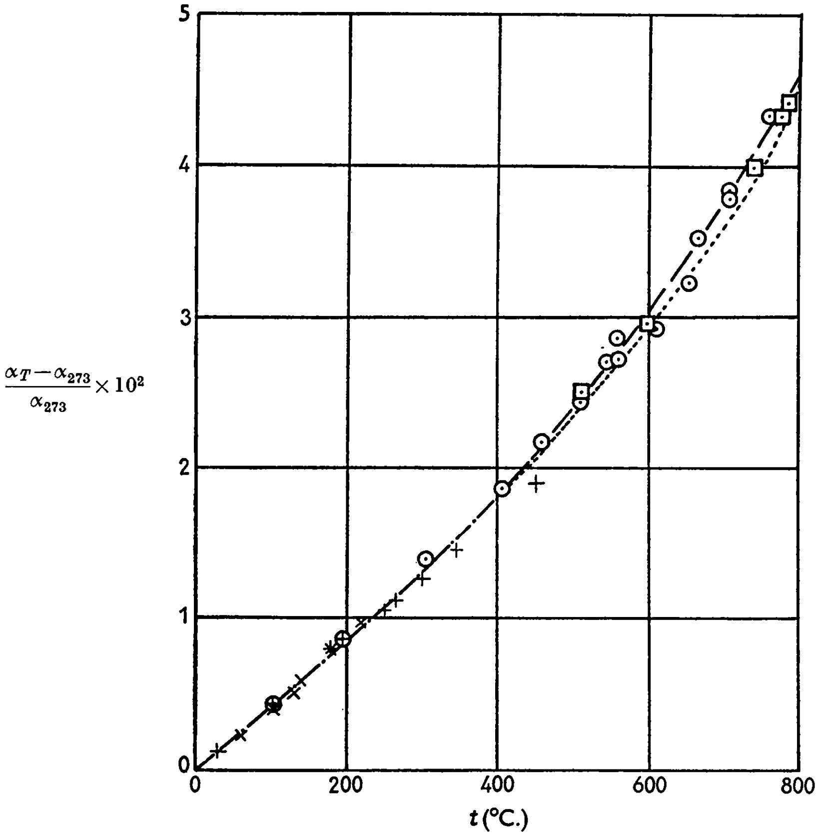

Fig. 1. Thermal expansion of NaCl.

○: present measurements (Debye camera); ⊡: present measurements (diffractometer); ×: Saïni (1934); +: Basu & Maitra (1938); — —: dilatometric measurements (smoothed), Eucken & Dannöhl (1934); ----: dilatometric measurements (smoothed), Walther, Haschkowsky & Strelkow (1937).

20–190° C. However, the concentration of lattice defects increases exponentially with temperature, so that the effect should be much more notable at high temperatures. In the course of the present work it was found that the observed expansion of NaCl and of the other alkali halides for which measurements have been published can be explained without recourse to lattice defects, viz. as a corollary of the anharmonicity of thermal vibration.

Experimental

A commercial preparation of NaCl (Merck, p.a.) was used. The results are presented in Fig. 1, which shows the relative increase of the cell constant, referred to its value at 0° C., as a function of temperature. Circled points refer to measurements with Cu K radiation in a one-sided Debye–Scherrer heating camera* of 4·55 cm. film radius. The camera takes six exposures on one film, and expansion values were derived from the displacements of all measurable lines on each film. Line positions (with respect to fiducial marks) could be determined reproducibly to within ±0·003 mm., the measurements being made on photographic contact prints (on glass plates) rather than on the original films, to avoid non-uniform contraction of the film under the slight heating action of the measuring projector. Each film was measured five times. The eccentricity error, as determined from the angular dependence of the ratios $\sin^2\theta_{hkl}:\sin^2\theta_{h'k'l'}$, was practically independent of temperature.

The accuracy of temperature measurement is believed to be well within ±5° C. The thermocouple used for the measurement and control of temperature had been calibrated under working conditions against the melting points of c.p. grade acetanilide (115° C.), saccharin (228° C.), $NaNO_3$ (310° C.), KNO_3 (335° C.), Sb (630·5° C.), KCl (770° C.) and NaCl (800° C.) by visual observation of the fusion of samples placed in the sample holder of the camera.

The experimental points indicate a considerable departure from linearity, especially near the melting point. Because of the theoretical importance of this phenomenon, this was checked by independent measurements with a furnace-equipped diffractometer* of different geometry (squares in Fig. 1).

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* Both the Debye–Scherrer heating camera and the diffractometer used in this investigation have been designed by Prof. G. Hägg and were constructed in the workshop of the Institute.

X-ray measurements at intermediate temperatures have been reported by Saïni (1934) and by Basu & Maitra (1938); they are incorporated in Fig. 1 for comparison. The design of the furnace used by Basu & Maitra suggests the existence of a temperature gradient between the thermocouple and the surface of the crystal that reflected the X-rays, which would explain the discrepancy between their higher-temperature points and the present measurements.

The 'macroscopic' thermal expansion of NaCl at high temperatures has been measured by Eucken & Dannöhl (1934) and by Walther, Haschkowsky & Strelkow (1937). The curves in Fig. 1 are calculated from their empirical formulae for the 'true' coefficient of expansion, assuming the definition employed by these authors to be

$$\alpha = \frac{1}{l_T} \cdot \frac{dl}{dT} \,. \qquad (1)$$

The role of lattice defects

Although no extreme accuracy is claimed for the present measurements, they certainly confirm the non-linearity of the expansion observed in the dilatometric investigations quoted above.

The non-linear expansion of the silver halides observed by Strelkow (1937) has been interpreted as due to lattice defects by Lawson (1950), who found that the 'anomalous' expansion δ (= total expansion, $\Delta l/l_r$, minus 'regular' expansion extrapolated from room temperature, $\alpha_r[T-T_r]$) yields a linear logarithmic plot against $1/T$ so that

$$\delta = \frac{l_T - l_r}{l_r} - \alpha_r[T-T_r] = A \exp\left[-E_\delta/RT\right]. \qquad (2)$$

This expression is of the same form as that for the number of lattice defects in equilibrium at the temperature T. Lawson obtained good agreement between E_δ and the activation energy of ionic conductivity for AgBr, but not for AgCl. To account for the strong volume effect, he assumed the defects to be of the Schottky type, although Wagner & Beyer's (1936) finding of equal pycnometric and X-ray densities near the melting point spoke strongly in favour of Frenkel defects. This latter result has since been verified by Berry (1951), who found the lattice expansion of AgBr to agree within experimental error with Strelkow's data.

For NaCl a claim similar to Lawson's has been made by Uno (1951). However, the agreement between macroscopic and lattice dilatation found in the present work rules out any appreciable contribution of Schottky defects to the expansion of this salt, so that the non-linearity of the expansion could only be caused by Frenkel defects. In the first place the existence of Frenkel defects in the alkali halides is rather unlikely (cf., for example, Mott & Gurney, 1940; Jost, 1952), and the comparison of conductivity and expansion data in Table 1 shows that neither sort of electrically conducting defect can account for the observed non-linearities. This holds for all the alkali halides for which published data permit the comparison. It should be mentioned that the plots of equation (2) from which the activation energies E_δ were determined all deviate more or less from linearity, which in itself speaks against the underlying hypothesis.

(In separating the 'anomalous' and the 'regular' part of the expansion the choice of the 'regular' coefficient of expansion becomes rather critical when different substances are to be compared. Lawson's choice of the room-temperature value, α_{293}, is theoretically unsound. On the basis of Grüneisen's theory (1912, 1926) α cannot be expected to become strictly constant at any particular temperature, but it will cease to vary strongly at temperatures slightly above the Debye characteristic temperature θ. However, the choice of α_θ instead of α_{293} does not eliminate the

Table 1. *Comparison of thermal expansion and ionic conductivity data*

		Activation energies (kcal./g.-ion)			Concentration of lattice defects at melting point		
	Temperature of fusion, t_f (°C.)	Conductivity E_σ	Expansion[a]		Conductivity $(n/N)_{T_f} \times 10^2$	Anomalous volume expansion[g]	
			$E_\delta^{(\theta)}$	$E_\delta^{(273)}$		$3\delta_{T_f}^{(\theta)} \times 10^2$	$3\delta_{T_f}^{(273)} \times 10^2$
LiF	848	30·8[b]	10·0	5·2	0·04[b]	2·6	4·8
NaCl	800	22·8[c]	6·9	6·9	0·01[f]	3·6	3·6
KCl	770	23·8[c]	5·2	5·4	0·01[c]	4·2	3·8
KBr	730	23·0[c]	5·2	6·3	—	3·4	3·1
KI	681	17·6[c]	4·8	5·8	—	4·5	3·6
AgCl	455	12[d]	5·8	7·2	0·6[d]	1·9	1·7
AgBr	430	10[d]	10·9	12·5[e]	2[d]	5·5	4·8[e]

a: For references to expansion measurements and for characteristic temperatures see Table 2.
b: Haven, 1950.
c: Jacobs & Tompkins, 1952.
d: Mott & Gurney, 1940.
e: Lawson (1950) gives different values, the difference being due to misprints in Stelkow's paper, to the non-linearity of the plot of equation (2) and to the choice of a different temperature of fusion.
f: Etzel & Maurer, 1950.
g: In the case of Schottky defects, the volume expansion should be of the same order of magnitude as the concentration of defects; in the case of Frenkel defects, it should be *less* (cf. Lawson, 1950).

discrepancies in Table 1. In fact, it often results in still less linear plots of log δ against $1/T$.)

For the activation energies, the disagreement is within a factor of about 5. The concentrations of defects derived from conductivity data, however, are too low by several powers of ten to account for the observed 'anomalous' expansions. As a matter of fact, they are too low to give positively detectable expansion effects with the present state of both X-ray and dilatometric instrumentation, which is in full agreement with the present experimental results.

Thus, lattice defects cannot be responsible for the non-linearity of the thermal expansion, and it will be necessary to look for another explanation.

Comparison with Grüneisen's theory

Unfortunately, there is as yet no strict theory of the thermal expansion at high temperatures. Only an approximate treatment, based on the Debye model of a monatomic solid with a single characteristic temperature θ, has been developed by Grüneisen (1912, 1926) and Debye (1914). Starting from the picture of a crystal whose atoms exert nearly harmonic vibrations in an asymmetrical force field, the theory predicts a volume increase according to the relation

$$3\frac{a_T-a_0}{a_0}=\frac{V_T-V_0}{V_0}=\frac{E/Q}{1-p.E/Q}, \tag{3}$$

where E is the vibrational energy which can be represented by a Debye function, $E = 6RT.D(\theta/T)$; p and Q are constants which can be estimated from other properties of the crystal, cf. equation (6) below. Since this estimation implies a number of extrapolations, they were determined graphically using the inverted form of (3):

$$\frac{a_0}{a_T-a_0}=\frac{Q}{2R}\cdot\frac{1}{T.D(\theta/T)}-3p\,. \tag{4}$$

The left side is the reciprocal of the dilatation referred to 0° K.; to calculate this from the available dilatation data which are referred to 273° K., it is necessary to know $(a_{273}-a_0)/a_0$. This quantity can be estimated from the low-temperature approximation to (3):

$$3\frac{a_{273}-a_0}{a_0}\approx\left(\frac{E}{Q}\right)_{273}\approx\left(\frac{3\alpha E}{C_V}\right)_{273}=\frac{3\alpha_{273}.273.D(\theta/273)}{C(\theta/273)}, \tag{5}$$

where $C(\Theta/T)$ is the Debye specific heat function. The approximation $C_V/3\alpha = Q =$ constant is admissible at low temperatures. For the alkali halides, the dilatation from absolute zero to room temperature has been tabulated by Born & Huang (1954), who used a different approximation for Q. Their values are in fair agreement with those obtained from (5).

Fig. 2 shows the 'Grüneisen plots' obtained with equation (4) for the alkali halides. The parameters θ, $3p$ and $Q/2R$ are listed in Table 2. The characteristic temperatures are taken from a compilation of experimental determinations by Lonsdale (1948); figures

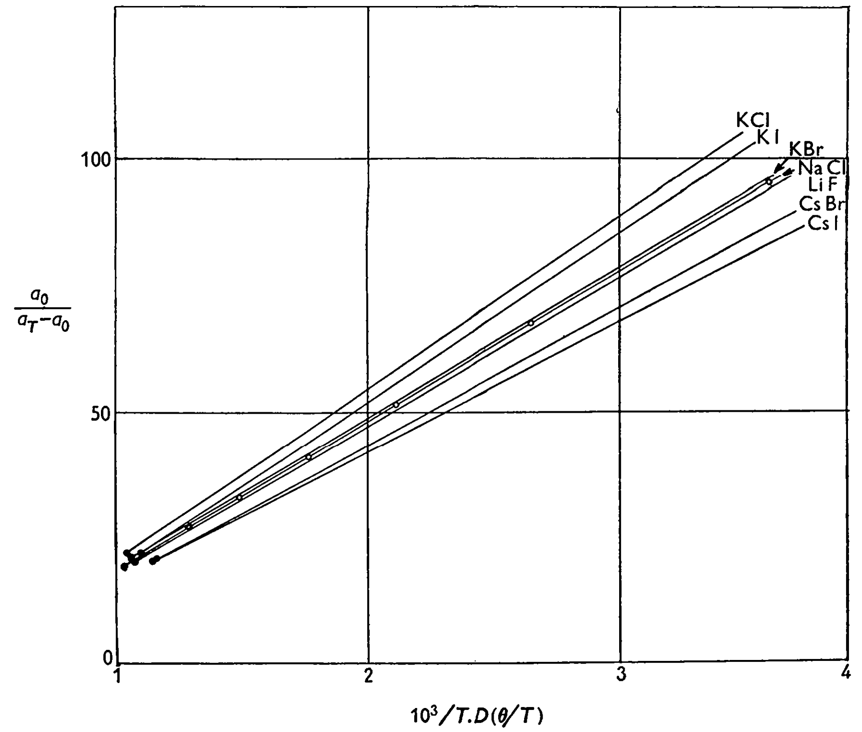

Fig. 2. Grüneisen plots (equation (4)) for some alkali halides. Full circles: melting points; empty circles: Eucken & Dannöhl (1934). (Only points for NaCl are set out in the figure.)

Table 2. *Grüneisen parameters* (*cf. equation* (4)) *for some alkali halides*

	$3p$ from Fig. 2	$Q/2R$ from Fig. 2	$Q/2R$ (equation (6))	Reference* (expansion data)	θ (°K.)
LiF	11·5	$29{\cdot}4\times10^3$	$26{\cdot}2\times10^3$	E. & D.	(558)
NaCl	11·0	$29{\cdot}5\times10^3$	$28{\cdot}2\times10^3$		281
KCl	13·0	$33{\cdot}9\times10^3$	$31{\cdot}1\times10^3$		227
KBr	9·0	$28{\cdot}4\times10^3$	$28{\cdot}6\times10^3$		177
KI	13·9	$32{\cdot}8\times10^3$	$25{\cdot}2\times10^3$		132
CsBr	10·8	$27{\cdot}1\times10^3$	$23{\cdot}2\times10^3$	J. A. & B.	(114)
CsI	9·2	$25{\cdot}7\times10^3$	$22{\cdot}3\times10^3$		95

* E. & D.: Eucken & Dannöhl, 1934.
J. A. & B.: Johnson, Agron & Bredig, 1955.

in brackets are extrapolated from Lindemann's formula (1910), the constant of which was adapted to give the best fit with experimentally determined values from the alkali halide group. With the parameters of Table 2 the expansions of the alkali halides can be represented to within a few parts in a thousand in the high-temperature region and to a few parts in a hundred at lower temperatures, where the uncertainty inherent in the estimation of $(a_{273}-a_0)/a_0$ becomes important.

Table 2 contains even values of $Q/2R$ calculated from the relation (Grüneisen, 1912, 1926)

$$Q = V_0/\gamma\beta_0\,, \tag{6}$$

with $R = 8{\cdot}315\times10^7$ erg mole^{-1}. deg.$^{-1}$, and values of the constant γ, the compressibility (β_0) and molar volume (V_0) at absolute zero taken from Born & Huang (1954). It will be noted that Q from equation (6) is mostly too low, the difference being greatest for KI and for the cesium salts, where strong polarization occurs. On the whole, the agreement is quite fair.

The theoretical estimation of $3p$ is much less certain. Assuming an interatomic potential of the form $\Phi = -Ar^{-n}+Br^{-m}$, Grüneisen (1912, 1926) gives $3p = (m+n+3)/2$, or 6·5 for the alkali halides. This potential law is known to be incorrect, so that the disagreement with the experimental values in Table 2 is not surprising.

Thus, Grüneisen's theory not only predicts the correct type of expansion curve for the alkali halides, but even the quantitative agreement is as good as the crudity of the theoretical approach would lead one to expect.

In conclusion, attention may be drawn to the crowding-together of the end points of all the lines in Fig. 2. For all alkali halides *melting* occurs when the vibrational energy and the thermal expansion (i.e. the amplitudes of thermal vibration) have reached a certain limit. This fact forms the basis of the validity of a number of semi-empirical relations such as the Lindemann formula or the rule $\bar{\alpha}.T_f \approx$ const. (Grüneisen, 1912, 1926). A discussion of the melting mechanism of the alkali halides on this basis, with references to previous work, has been given by Thompson (1953).

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