

# High-Temperature Thermal Expansion of Rocksalt\*

M. F. MERRIAM,<sup>†</sup> R. SMOLUCHOWSKI,<sup>‡</sup> AND D. A. WIEGAND  
*Carnegie Institute of Technology, Pittsburgh, Pennsylvania*

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It is shown that the temperature dependence of the thermal expansion of NaCl, at temperatures above 500°C, can be related to the concentration of thermally generated Schottky defects. The thermal expansion is considered to consist of two terms; a "normal" contribution and an "anomalous" part; the latter includes the effect of vacancies upon the potential of the lattice in their immediate vicinity. The magnitude of the "anomalous" contribution increases exponentially with temperature with an activation energy consistent with that deduced from ionic conductivity studies.

POINT defects generated in rocksalt by x-ray irradiation give rise to increases in the linear thermal expansion coefficient which are an order of magnitude greater than the defect concentrations.<sup>1</sup> It is well established that point defects are generated thermally at high temperatures in NaCl, and these defects are known to be Schottky pairs. The spatial distribution of the vacancies is generally taken to be random, there being no positive evidence for aggregation. One would expect then that these thermally generated defects, in addition to increasing the volume of the crystal, would also increase the thermal expansion coefficient of rocksalt at high temperatures. This increase would be proportional to the increase in defect concentration which can be deduced independently from the conductivity measurements of Etzel and Maurer.<sup>2</sup>

In both the alkali halides and the silver halides the thermal expansion coefficient increases with temperature and the increase becomes more rapid as the melting point is approached. Some years ago Lawson<sup>3</sup> suggested that the observed rapid increase in the thermal expansion coefficient of AgCl and AgBr at temperatures approaching the melting point reflected the thermodynamic generation of point defects. This has since been confirmed by the experiments of Zieten,<sup>4</sup> who measured expansivity as a function of the temperature for AgCl and AgBr doped with various concentrations of divalent positive ions. Zieten was able to draw conclusions regarding the type of disorder in these salts by supposing that each point defect contributed to the observed expansion by virtue of its own volume. Thus a Frenkel defect can be distinguished experimentally from a Schottky defect because it produces a smaller observed expansion.

A suggestion similar to Lawson's has been made by Uno<sup>5</sup> for NaCl. The "anomalous" increase in expansion is much less pronounced in alkali halides than in the

silver halides, however, and Uno's proposal has been disputed by Fischmeister<sup>6</sup> who concluded that the observed temperature dependence of the expansion coefficient could be fully accounted for within the Grüneisen theory. Fischmeister ruled out any appreciable contribution of Schottky defects to the expansion of the salt on two grounds: (1) His x-ray measurements showed the lattice dilatation to be in substantial agreement with the macroscopic expansion; and (2) the concentration of defects in NaCl derived from high-temperature conductivity data is too low by several orders of magnitude to account for the observed expansion. There is also a discrepancy in the activation energy.

Fischmeister's conclusion that the observed temperature dependence of the thermal expansion coefficient  $\alpha$  accounted for within the Grüneisen theory has been questioned by Fletcher,<sup>7</sup> who showed that the graphical analysis used by Fischmeister was too insensitive to allow a definite statement. Fletcher's calculation<sup>8</sup> of the temperature dependence of  $\alpha$  in NaCl showed the Grüneisen theory to be in poor agreement with experiment. A more refined calculation of the thermal expansion by Eastabrook<sup>9</sup> may have improved the agreement at high temperature, but does not allow a numerical comparison with experiment. It will be shown below that an agreement with experiment can be obtained by supposing that defects do play a role in the high-temperature expansion, and that at least part of the increase in  $\alpha$  at high temperature can be accounted for in this way.

In NaCl the thermal expansion coefficient, on the Grüneisen theory, should be a reasonably slowly varying function of temperature at temperatures above the Debye temperature, which is only a few degrees above room temperature. The Grüneisen contribution to the high-temperature thermal expansion of the crystal can be, therefore, represented by taking only the linear term in a power series expansion, and writing

$$\alpha(T) = \alpha(T_0) + \left( \frac{d\alpha}{dT} \right)_{T=T_0} (T - T_0) + \Delta\alpha,$$

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<sup>†</sup> Now at the University of California, La Jolla, California.

<sup>‡</sup> Now at Princeton University, Princeton, New Jersey.

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<sup>2</sup> H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

<sup>3</sup> A. W. Lawson, Phys. Rev. **78**, 185 (1950).

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<sup>5</sup> Y. Uno, Busseiron Kenkyu **36**, 32 (1951) [cf. Chem. Abstracts **46**, 6890i (1952)].

<sup>6</sup> H. F. Fischmeister, Acta Cryst. **9**, 416 (1956).

<sup>7</sup> G. C. Fletcher, Phil. Mag. **2**, 639 (1957).

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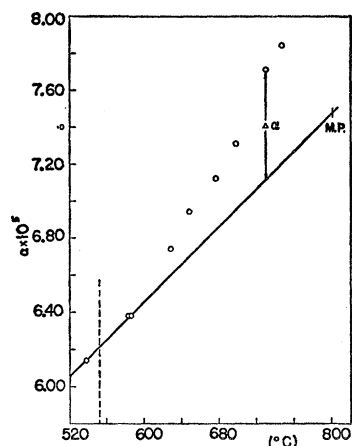


FIG. 1. Temperature dependence of the thermal expansion coefficient of NaCl. The dashed vertical line indicates the estimated position of the extrinsic-intrinsic transition. Data of Eucken and Dannöhl.

where  $\alpha(T)$  is the linear coefficient of thermal expansion at some temperature  $T$  between  $T_0$  and the melting point, and  $\Delta\alpha$  the "anomalous" part, is a contribution arising from the defects generated thermally at high temperatures. Since thermally generated defects are randomly distributed in the crystal, and since  $n/N$ , the defect concentration, is only of the order  $10^{-4}$  even at the melting point, we expect a linear relationship  $\Delta\alpha = bn$ , where  $b$  is a constant characteristic of the average effect of a vacancy upon the expansion coefficient. The thermally generated defects will not be important so long as they are fewer in number than those already present in the crystal as a result of impurities. We cannot, therefore, expect any recognizable temperature variation in  $\Delta\alpha$  at temperatures below  $T_0$ , the "knee" of an electrical conductivity vs  $1/T$  plot, but above this temperature  $\Delta\alpha$  should increase exponentially with the temperature with an activation energy corresponding to that for the formation of Schottky pairs.

The electrical conductivity of the crystals on which the expansion measurements were made was not measured, but assuming that the over-all degree of purity was about the same as that of the crystals used in the conductivity measurement of Etzel and Maurer, one obtains 550–575°C as a reasonable choice for  $T_0$ . Figure 1 shows the data of Eucken and Dannöhl<sup>10</sup> for the high-temperature region. A reasonable tangent to the curve of  $\alpha(T)$  vs  $T$  can be drawn at  $T_0$  and  $\Delta\alpha(T)$  obtained graphically as shown. The values of  $\Delta\alpha$  thus obtained are shown on the appropriate semilogarithmic plot in Fig. 2. It is seen that they can be fitted quite well to a straight line having a slope corresponding to  $\frac{1}{2}W_s$ , where  $W_s = 2.02$  ev, which is the value of the activation energy for Schottky pair formation as determined by Etzel and Maurer.

An estimate of the concentration of defects  $n/N$  at the melting point can be obtained from the equation  $\sigma = ne\mu$ , using the conductivity data of Etzel and Maurer and the mobility data either of Etzel and Maurer or of

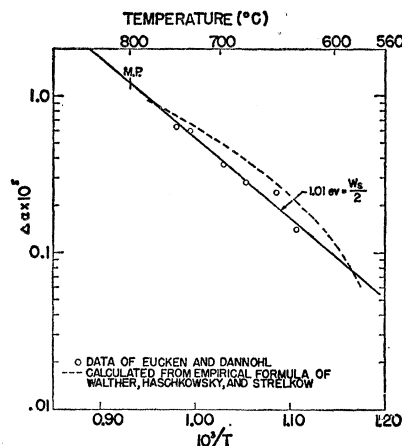


FIG. 2. The postulated defect contribution to the thermal expansion coefficient vs reciprocal temperature as taken from Fig. 1.

Read and Katz.<sup>11</sup> This leads to  $n/N = 10^{-4}$  whereas  $\Delta\alpha/\alpha$  at the meeting point, from Fig. 2, is approximately 0.15. The equation  $\Delta\alpha/\alpha = 14n/N$ , found to apply for radiation-induced defects,<sup>1</sup> is therefore not satisfied for thermally generated defects by two orders of magnitude. This is not too surprising since the pre-exponential factors in  $\mu$ ,  $\sigma$ , and  $\Delta\alpha$  are very sensitive to the values chosen for the respective activation energies, and difficult to determine with precision. Furthermore, the spatial distribution and type of defects induced by irradiation may not be those prevailing at high temperatures in the un-irradiated salt. Additional measurements of  $\alpha$ , and a more sophisticated theoretical separation of the "normal" and "anomalous" contributions to  $\alpha$  may clear up this difference.

The expansion data of Walther *et al.*<sup>12</sup> show considerable scatter, making the graphical method of analysis impractical. If the empirical formula with which they represent all their data is used, setting  $T_0 = 552^\circ\text{C}$ , then the curve shown dashed in Fig. 2 is obtained for  $\Delta\alpha$  as a function of  $T$ . This also represents a satisfactory fit to the indicated straight line, since one would expect a systematic deviation from linearity for an empirical formula. Furthermore, it appears on close inspection that the high-temperature data fit the straight line of Fig. 2 better than the empirical formula.

The x-ray data of Fischmeister are not accurate enough to detect the non-linearity in  $\alpha$  at high temperature. They are also not accurate enough (and neither are the macroscopic dilatation measurements) to observe any difference between the macroscopic expansion and the expansion calculated from the measured increase in the lattice parameter. No difficulty arises regarding the required concentration of defects since the thermally generated Schottky defects contribute

<sup>11</sup> P. L. Read and E. Katz, *Phys. Rev. Letters* **5**, 466 (1960).

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to the thermal expansion almost entirely by virtue of the effect of the vacancies on the interionic potential. The additional sites created at the surface do not make a significant contribution (less than 1%) to the expansion of the crystal, as Fischmeister has noted.

The available expansion data for NaCl are just barely accurate enough to provide basis for the conclusions

here drawn. It should be kept in mind that the contribution of the defects is a *third-order* effect in the measured variable. Additional careful expansion measurements in the high-temperature range, both for NaCl and for other alkali halides, with simultaneous measurement of the high-temperature electrical conductivity, would be very desirable.

## Theory of Field Emission from Semiconductors

ROBERT STRATTON

Central Research Laboratories, Texas Instruments Incorporated, Dallas, Texas

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The field emission current density  $j_e$ , originating from the conduction band, is derived for an arbitrary degeneracy (i.e., Fermi energy) at the surface. The theory allows for a difference between the effective and free electron masses; detailed results being worked out for spherical energy surfaces. Simple formulas for  $j_e$  are presented which involve correction factors that are slowly varying functions of the temperature, field  $F$ , and Fermi energy, and have been computed numerically;  $j_e$  is approximately proportional to the emission probability of an electron either at the Fermi level or at the bottom of the conduction band for positive or negative Fermi energies, respectively. Strong deviations from linearity, of a  $\ln j_e$  versus  $(1/F)$  plot, require that the Fermi energy at the surface depend markedly on  $F$ . The emission current for the intermediate, or  $T$ - $F$ , range is also considered. The field emission current density  $j_v$  originating from the valence band is also discussed. As an example, numerical results are given for germanium. For this case,  $j_v$  exceeds  $j_e$  at room temperature, except when the surface is strongly degenerate  $n$  type. The theory is qualitatively consistent with Allen's experimental results for a clean germanium surface.

### I. INTRODUCTION

IF a sufficiently intense electric field is applied normal to the surface of a metal or semiconductor, electrons will be emitted, through the surface potential barrier, by the quantum mechanical tunnelling effect. Since the fields required for a measurable current emission are in the range  $10^7$  to  $10^8$  v/cm, the experimental arrangement usually consists of a fine needle emitter (radius of curvature of the tip about  $10^{-4}$  cm) placed inside an evacuated chamber, partly lined with a conducting film which collects the electrons. If the surface of the collector, or anode, is also treated with a fluorescent material, characteristic patterns are observed from nearly clean single crystal emitters (electron field emission microscope<sup>1</sup>).

The theory of field emission from metals was first derived by Fowler and Nordheim<sup>2</sup> in 1928, who showed that if the temperature is not too high, most of the emitted electrons originate from a small energy interval around the Fermi level of the metal. At the other extreme, high temperatures and low fields, electron emission over the potential barrier, rather than through it, predominates, i.e., thermionic emission. There is also an intermediate range of fields and temperatures where the electrons tunnel through the barrier but come mainly

from energy levels well above the Fermi level in the metal.<sup>3</sup> This process has been called  $T$ - $F$  emission by Dolan and Dyke.<sup>4</sup> Experimental and theoretical progress in field emission from metals has recently been reviewed by Good and Müller.<sup>5</sup>

When the theory of field emission from semiconductors was considered by the present author in 1955,<sup>6</sup> there had only been preliminary experimental observations of this effect, using<sup>7</sup> Cs<sub>3</sub>Sb and the photoconductors CdS and CdSe.<sup>8</sup> Since then there have been experimental studies of field emission from CdS,<sup>9</sup> CdSe,<sup>9</sup> W<sub>2</sub>C,<sup>10-12</sup> Mo<sub>2</sub>C,<sup>11</sup> SiC,<sup>13</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>14</sup> SiO<sub>2</sub>,<sup>14</sup> ZnS,<sup>15</sup> Te,<sup>16</sup>

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