

A Reformulation of the Temperature Dependence of the Debye Characteristic Temperature and its Effect on Debye–Waller Theory

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Zener & Bilinsky have explained the observed high-temperature deviations from the Debye–Waller theory of the temperature dependence of the intensity of X-ray diffraction spectra in terms of the changes in Θ , the Debye characteristic temperature, as the temperature is raised. Their formulation for the temperature dependence of Θ is in terms of an empirical constant and the lattice enthalpy. We here give an alternative formulation in terms of the Grüneisen constant and the volume. The two formulations of the temperature dependence of Θ are found to yield approximately the same results for NaCl and KCl. The Debye–Waller factor has also been modified so as to yield a relationship linear in a reduced temperature scale that compensates for the change in Θ as the temperature is changed. The X-ray data when appropriately plotted do yield a straight line in agreement with the modified Debye–Waller factor. The slope of the straight line can be used to find the room-temperature value of Θ . The values found for NaCl and KCl are in reasonable agreement with values for Θ obtained from specific-heat measurements.

Introduction

Although the current theoretical trend (Peierls, 1955) is to take the Debye model as only a qualitative model of the thermal properties of crystal lattices, nevertheless in practice the Debye model does serve as a useful semi-empirical procedure for correlating various thermal data. It is therefore surprising that the Debye–Waller theory of the temperature dependence of the intensity of the X-ray diffraction spectra seriously deviates from theory at higher temperatures (James & Firth, 1927; James & Brindley, 1928). Zener & Bilinsky (1936) have adequately explained the deviations in NaCl (James & Firth, 1927) and KCl (James & Brindley, 1928) in terms of the changes in the Debye characteristic temperature Θ as the temperature is raised. Their resulting expression for $\Theta(T)$ is in terms of an empirical constant (approximately equal to the constant appearing in the Nernst–Lindemann equation) and the lattice enthalpy. We shall here give an alternative formulation of the temperature dependence of the Debye characteristic temperature in terms of the Grüneisen constant and the volume (in some respect similar to a formulation of Owen & Williams (1947) in terms of the Einstein characteristic frequency). The main advantages of the present method are: it is easier to measure volume as a function of temperature than enthalpy, hence more volume data are available; it avoids some of the complications which arise in separating the lattice enthalpy from the total enthalpy in cases where there are electronic and magnetic contributions to the total enthalpy (Hofmann, Paskin, Tauer & Weiss, 1956).

Theory

In Debye theory it is assumed that the volume of the crystal remains constant as the temperature changes.

In actual practice the pressure remains constant and the volume changes owing to thermal expansion. Thus, it is to be expected that Θ , which depends explicitly on volume (Fowler, 1955), will in turn vary with temperature. If $\Theta(T)$ is defined as the characteristic Debye temperature the crystal would exhibit if it were first expanded at $T = 0$ from volume V_0 to V_T and then brought to temperature T at constant volume V_T , it follows that $\Theta(T)$ is equal to $\Theta(V_T)$. Thus, the problem of finding Θ as a function of temperature can equivalently be solved in terms of the variation of Θ as a function of the volume. Leaving for the Appendix the mathematical details, the following equation is obtained for $\Theta(V_T)$ in terms of the volume and the Grüneisen constant γ :

$$d \ln \Theta(V_T)/dV = -\gamma V^{-1}. \quad (1)$$

From the approximate constancy of γ over the range of temperature of interest and the corresponding range of volume of interest, it is deduced that γ is likewise approximately independent of volume. Integrating (1), we find

$$\Theta(V_T)/\Theta(V_{T_0}) = \Theta(T)/\Theta(T_0) = (V_{T_0}/V_T)^\gamma. \quad (2)$$

In practice, it is usually the linear expansion that is measured. For isotropic crystals, we therefore rewrite (2) as follows:

$$\Theta(T)/\Theta(T_0) = [l(T_0)/l(T)]^{3\gamma}. \quad (3)$$

Comparison of present formulation with that of Zener & Bilinsky

The relationship for the change in Θ with temperature found by Zener & Bilinsky (1936) is

$$\Theta(T)/\Theta(T_0) = \exp [-KH(T)], \quad (4)$$

where

$$K = (C_p - C_v) / TC_v C_p \quad \text{and} \quad H(T) = \int_{T_0}^T C_p dT.$$

We here compare the results of equations (3) and (4) for NaCl and KCl in the region from 0° C. to 600° C. The linear expansion data needed for (3) are taken from the *Handbook of Physical Constants* (Birch, Schairer & Spicer, 1942) and the values for the Grüneisen constant from Slater (1939). The results for the Zener-Bilinsky equation are taken from their paper. A comparison of the results is given in Table 1.

Table 1. Comparison of $-\ln [\Theta(T)/\Theta(T_0)]$ as a function of the temperature T ° C. as calculated for KCl and NaCl from the Zener-Bilinsky enthalpy formulation and the present volume formulation

The reference temperature is $T_0 = 0$ ° C. and the reference Θ is likewise $\Theta(T = 0$ ° C.)

	T (°C.)	0	100	200	300	400	500	600
KCl	Enthalpy	0	0.017	0.035	0.053	0.072	0.089	0.11
	Volume	0	0.017	0.033	0.055	0.075	0.10	0.13
NaCl	Enthalpy	0	0.019	0.039	0.058	0.078	0.099	0.12
	Volume	0	0.021	0.041	0.065	0.089	0.11	0.13

It can be seen that the volume and enthalpy formulation yield almost identical results.

Revised Debye-Waller factor

Zener & Bilinsky (1936) have already shown that if the explicit temperature dependence of Θ is inserted in the Debye-Waller formula, the general features of the temperature dependence of the X-ray data for NaCl and KCl are reproduced. As our formulation yields equivalent results, use of equation (3) in the Debye-Waller formula will likewise reproduce experiment*. We shall here further show that it is possible to modify the form of the Debye-Waller factor so that the X-ray intensities ρ when plotted against a reduced temperature T' yield a straight line whose slope is simply related to Θ .

We first limit ourselves to the region $T \geq \Theta$ and thus write $2M$, the Debye-Waller factor (in terms of the notation of James (1954)) as

$$2M = \frac{12h^2 \sin^2 \theta T}{mk\lambda^2 \Theta^2(T)}. \quad (5)$$

* It should be noted that Owen & Williams (1947) erroneously insert the relationship for the temperature dependence of the Einstein characteristic frequency or equivalent temperature in the Debye-Waller formula derived explicitly for the Debye model of a solid and hence defined in terms of the Debye characteristic temperature. Fortunately, the relative temperature dependence of the Einstein and Debye characteristic temperatures are the same. Hence, Owen & Williams's empirical treatment of their data, which depends only on the relative change in the Debye characteristic temperature, is valid despite their interchange of Einstein and Debye characteristic temperatures.

Introducing $\Theta(T)$ as given in (2), equation (5) can be written as

$$2M = \frac{12h^2 \sin^2 \theta}{mk\lambda^2 \Theta^2(T_0)} \left(\frac{V_T}{V_{T_0}} \right)^{2\gamma} T. \quad (6)$$

Thus, $2M$ is seen to be proportional to the reduced temperature $T' = T(V_T/V_{T_0})^{2\gamma}$. As the intensity ρ of a given spectrum is proportional to $\exp(-2M)$, it follows that

$$\ln \frac{\rho_T}{\rho_{T_0}} = - \frac{12h^2 \sin^2 \theta}{mk\lambda^2 \Theta^2(T_0)} (T' - T'_0). \quad (7)$$

From (7) it is evident that a plot of $\ln(\rho_T/\rho_{T_0})$ versus T' should yield a straight line. In Figs. 1(a) and 1(b),

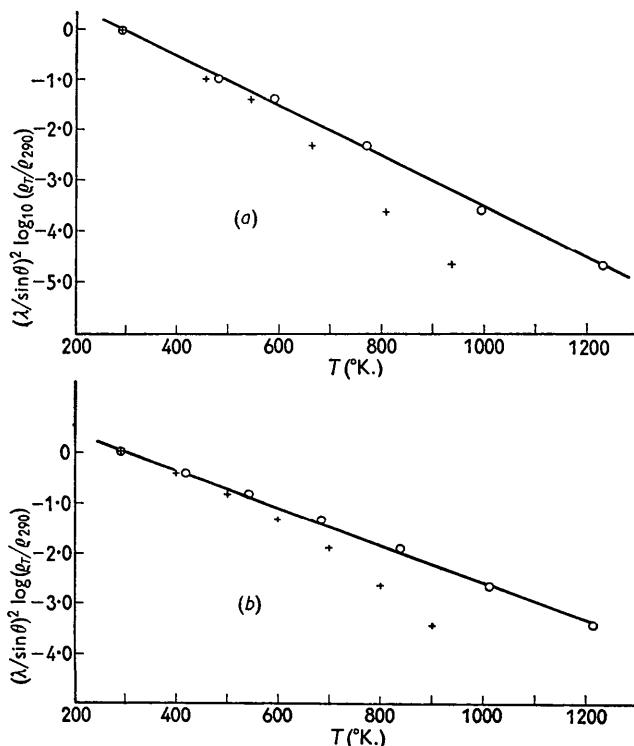


Fig. 1. (a) Comparison of plots of the logarithm of the ratios of the X-ray intensities from the 400 spectra of KCl versus the measured temperature and the reduced temperature. The circles correspond to the data plotted against the reduced temperature and the crosses to the data plotted against measured temperature. The straight line drawn through the data corresponds to a room-temperature value of $\Theta = 231$ ° K. (b) Comparison of plots of the logarithm of the ratios of a set of X-ray intensities from the spectra of NaCl versus the measured temperature and the reduced temperature. The circles correspond to the data plotted against the reduced temperature and the crosses to the data plotted against the measured temperature. The straight line drawn through the data corresponds to a room-temperature value of $\Theta = 302$ ° K.

we compare the KCl data (James & Brindley, 1928) and NaCl data (James & Firth, 1927) as plotted versus T and T' , taking $T_0 = 290$ ° K. as the reference temperature. It can be seen that the data better ap-

proximate a straight line when plotted versus T' , in accord with equation (7) based on the explicit temperature dependence of Θ . It might be noted that the agreement with theory is better for KCl than NaCl. This is not surprising when it is realized that the theory as such is derived for a monatomic crystal rather than the binary compounds here treated. In the case of KCl the masses are almost equal and it may be treated as a simple solid. In the case of NaCl a more sophisticated treatment would require the data to be analyzed in terms of two characteristic temperatures (James & Firth, 1927), one for each atom type. In the absence of appropriate data over the temperature range to allow such a separation of the behavior of the two atom types, we have only been able to study the average effect (James & Firth, 1927). From the slope of the straight line on the reduced temperature plot, the room-temperature value of Θ can be found. The values obtained here are $\Theta(\text{KCl}) = 231^\circ \text{K.}$ and $\Theta(\text{NaCl}) = 302^\circ \text{K.}$, as compared to $\Theta(\text{KCl}) = 230^\circ \text{K.}$ and $\Theta(\text{NaCl}) = 281^\circ \text{K.}$ obtained from specific-heat data (James, 1954).

It is therefore concluded that the Debye-Waller theory, when modified to take into account the temperature dependence of the characteristic temperature, is a reasonable way of semi-empirically correlating the temperature dependence of X-ray diffraction intensities. In the light of the empirical nature of the Debye characteristic temperature it is further gratifying to find that Θ obtained from specific heat and X-ray measurements are in agreement.

APPENDIX

Although there are various derivations of $d\Theta/dV$ in the literature, for completeness we include an alternative derivation. $\Theta(V)$ can be expressed in terms of k , the compressibility and, β , the coefficient of volume expansion, by some simple manipulation of derivatives involving, p , the pressure, E , the energy and S , the entropy. These quantities are related as follows:

$$-p = \left(\frac{\partial E - TS}{\partial V} \right)_T = \left[\left(\frac{\partial E}{\partial \Theta} \right)_T - T \left(\frac{\partial S}{\partial \Theta} \right)_T \right] \frac{d\Theta}{dV}. \quad (\text{A-1})$$

Making use of the fact that in Debye theory, $E = \Theta F(\Theta/T)$ and $S = S(\Theta/T)$, equation (A-1) can be written as

$$-p = \left[E - T \left(\frac{\partial E}{\partial T} \right)_V + T^2 \left(\frac{\partial S}{\partial T} \right)_V \right] \frac{d \ln \Theta}{dV}, \quad (\text{A-2})$$

$$= E d \ln \Theta / dV. \quad (\text{A-3})$$

The simplification of (A-2) results from noting that $T(\partial S/\partial T)_V = (\partial E/\partial T)_V = C_V$. Taking the partial of p with respect to T , we further find that

$$-(\partial p/\partial T)_V = C_V d \ln \Theta / dV = -\beta/k, \quad (\text{A-4})$$

where

$$\beta = V^{-1}(\partial V/\partial T)_p \quad \text{and} \quad k = -V^{-1}(\partial V/\partial p)_T.$$

Θ is finally obtained as a function of the volume only, by introducing the Grüneisen relationship $\gamma = V\beta/C_V k$ into (A-4), yielding

$$d \ln \Theta / dV = -\gamma V^{-1}. \quad (\text{A-5})$$

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