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Theory of the Effect of Temperature on the Reflection of X-Rays by Crystals

III. High Temperatures. Allotropic Crystals

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In previous comparisons of the theoretical and experimental temperature effect for the reflection of x-rays, a marked discrepancy was found at high temperatures. It is here shown that this discrepancy disappears when proper account is taken of the variation of the characteristic temperature with temperature. Further, a relationship is found between the temperature factors for two allotropic modifications of the same element.

§1. INTRODUCTION

THE effect of temperature in decreasing the intensity of reflected x-rays has been surprisingly well interpreted at ordinary temperatures by the simple Debye model of a solid.[1] In this model the observed structure factor F is given by fe^{-M}, where f is the structure factor for a perfect lattice, and[1, 2]

$$M=\frac{6h^2T}{m_a k\Theta^2}\frac{\sin^2\theta}{\lambda^2}\phi\left(\frac{\Theta}{T}\right). \qquad (1)$$

Here m_a is the mean mass of the atoms, θ is the glancing angle of incidence of the x-rays on the reflecting plane, and ϕ is a factor which deviates appreciably from unity only when $\Theta/T>1$. If Θ is regarded as independent of temperature, as it has always been in the literature on x-rays, log F becomes a linear function of temperature in the region $T>\Theta$. The only experimental values of F at high temperatures are for NaCl[3] and for KCl.[4] The observed values of log F for these two crystals deviates radically from a linear function above 400°C. The purpose of the first part of this paper is to show that the temperature factor e^{-M} calculated by the simple Debye model is in agreement with the observed temperature factor even at high temperatures when proper account is taken of the variation of Θ with temperature.

While in §2 the continuous variation of M for a single crystal phase is discussed for the entire temperature range of that phase, in §3 the discontinuous variation of M is examined when the crystal undergoes an allotropic transformation.

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[1] See Compton and Allison, *X-Rays in Theory and Experiment*, pp. 435–445.

[2] For a simple derivation, see Zener and Jauncey, Phys. Rev. **49**, 17 (1936).

[3] James and Firth, Proc. Roy. Soc. **A117**, 62 (1928).

[4] James and Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

§2. TEMPERATURE FACTOR AT HIGH TEMPERATURES

The Debye model of a solid can make definite predictions about the temperature dependence of its properties only when the volume of the solid is kept constant. Thus in order to compare the observed specific heat with that predicted by the Debye model, C_p is always first reduced to C_V. In order fairly to compare with experiment the prediction of the Debye model as to the influence of temperature upon the intensity of reflected x-rays, proper account must be taken of the fact that the observations are made at constant pressure and not at constant volume.

Two methods of approach are available. In the first method, Eq. (1) is written in the form[1, 2]

$$M=8\pi^2\mu \sin^2 \theta/\lambda^2, \qquad (2)$$

where μ is the mean-square displacement of an atom. One then constructs a molecular model of the solid, including third- and fourth-order terms in the expression for the potential energy, which expands with temperature. Both C_p-C_V and the mean-square displacement μ are then directly calculated. This approach has already been investigated,[5] but has not given any quantitative predictions on the variation from the linear dependence of M with T at high temperatures.

In the second method of approach one starts from the phenomenological Debye model, and determines that dependence of Θ upon temperature which is necessary to fit the specific heat data. This function $\Theta(T)$ is then substituted into Eq. (1). This second method is the one adopted in this paper.

Two methods may be used to determine the function $\Theta(T)$ from specified heat data. The simpler one is to find that Θ which gives the observed C_V.[6] Thus $\Theta(T)$ is defined by the equation

$$C_V(T)=C_D\{\Theta(T)/T\}. \qquad (3)$$

The second method[7] is to determine that function $\Theta(T)$ which makes the observed entropy equal to the entropy calculated from the Debye model. The observed entropy (per atom) at a temperature T_0 is

$$S_{\text{obs.}}(T_0)=k\int_0^{T_0}\frac{C_p}{T}dT.$$

In order to calculate the entropy by the Debye model, one must pass from the absolute zero to the temperature T_0 in two steps. First one changes the volume of the solid, keeping it at the absolute zero, from its value at $p=0$, $T=0$, to its value at $p=0$, $T=T_0$. According to the Nernst heat theorem,[8] the entropy change is zero in this change of volume at the absolute zero. The solid is now heated, at constant volume, from $T=0$ to $T=T_0$. Throughout this second process the characteristic temperature remains constant. Hence the entropy change is given by

$$S_D(T_0)=k\int_0^{T_0}\frac{C_D\{\Theta(T_0)/T\}}{T}dT.$$

If we now equate these two expressions for the entropy, and differentiate with respect to T_0, we obtain

$$(d\ln\Theta)/dT=-(C_p-C_D(\Theta/T))/TC_D(\Theta/T). \qquad (4)$$

If the Debye model gave an exact representation of the specific heat, and if the empirical C_p and C_V were known precisely, Eqs. (3) and (4) would give the same function $\Theta(T)$. However, since $C_D(\Theta/T)$ becomes very insensitive to Θ when T becomes comparable with and larger than Θ, either a small error in the empirical values of C_V or a slight deviation of the true C_V from C_D produces a relatively large change in $\Theta(T)$. This is illustrated in Table I. The function $\Theta(T)$ obtained from Eq. (4) is not sensitive to these errors. The second method is thus used in this paper.

The integration of Eq. (4) only gives the ratio $\Theta(T)/\Theta(0)$. $\Theta(0)$ must be determined by using Eq. (3) at low temperatures. The function $\Theta(T)$ thus determined, when substituted into Eq. (1), gives the temperature factor at all temperatures

TABLE I. The second row gives the percent error in Θ due to a 1 percent error in C_V, when $\Theta(T)$ is determined from Eq. (3).

Θ/T	0.25	0.5	1	2	4
$\delta\ln\Theta/\delta\ln C_V$	240	35	9.5	2.7	0.8

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[5] I. Waller, Ann. d. Physik **83**, 153 (1927).

[6] Jauncey and Deming, Phys. Rev. **48**, 481 (1935).

[7] This method is in principle identical to that used by Fowler, *Statistical Mechanics*. The derivation here given is, however, simpler than that given by Fowler.

[8] M. Plank, *Treatise on Thermodynamics*, 5th edition, p. 274.

TABLE II. *Log of ratio $\Theta(T)/\Theta(0)$ for KCl and NaCl at various temperatures as given by Eq. (5).*

T (°C)	-200	-100	0	100	200	300	400	500	600
$-\ln\{\Theta(T)/\Theta(0)\}$ KCl	0.00346	0.0176	0.0341	0.0513	0.0690	0.0870	0.106	0.123	0.141
NaCl	0.00266	0.0160	0.0330	0.0519	0.0717	0.0911	0.111	0.132	0.153

with constant pressure as predicted by the Debye model.

According to the Debye model C_D and C_V are identical. Hence in Eq. (4) C_D may be replaced by C_V. Now it is well known that the ratio[9] $(C_p-C_V)/(TC_VC_p)$ is very nearly a constant over the entire temperature range of those solids with a simple structure, the only solids to which the Debye model is applicable. The constant K may be calculated from the known values of C_p and C_V at one temperature T_0, say at room temperature. When this relationship is used, the integration of Eq. (4) gives

$$\Theta(T)=\Theta(0)e^{-KH(T)}, \tag{5}$$

where

$$H(T)=\int_0^T C_p dT$$

and $K=[C_p(T_0)-C_V(T_0)]/TC_p(T_0)C_V(T_0)$.

The only experiments over a wide range of temperatures are for NaCl[3] and KCl.[4] The ratio $\Theta(T)/\Theta(0)$ obtained from Eq. (5) for these two crystals is given in Table II. The accepted values of $\Theta(0)$, which are obtained from Eq. (3), are 281°K for NaCl and 230°K for KCl. The comparison between the calculated and experimental values of log $F(T)/F(290°)$ is given in Figs. 1 and 2. A better fit with the experimental data is obtained by taking slightly larger values for $\Theta(0)$ than given by Eq. (3). The experimental points at the two highest temperatures for KCl fall considerably below the best theoretical curve. In view of the excellent fit with the other points, and in view of the increasing spread of the experimental points with temperature, these two isolated experimental points are probably too low.

It is to be expected that the $\Theta(0)$ which gives the best fit to the x-ray reflection data will always be somewhat larger than the $\Theta(0)$ determined from the specific heat data via Eq. (3). This is because on the Debye model the solid is strictly not specified by a single Θ. The Θ used in C_D and in Eq. (1) refers to an average Θ, but not to the same average. In the first case Θ refers to an average of the type $(\overline{\theta^{-3}})^{-\frac{1}{3}}$, in the second case to an average of the type $(\overline{\theta^{-2}})^{-\frac{1}{2}}$. Now it may readily be proved, by using Schwarz' inequality,[10] that

$$(\overline{\theta^{-3}})^2 \geqslant (\overline{\theta^{-2}})^3.$$

The application of this inequality to an elastically isotropic solid will now be considered. Here Θ as defined by the first average, say Θ_{C_V} is given by

$$\Theta_{C_V}{}^{-3}=(2\theta_t{}^{-3}+\theta_l{}^{-3})/3,$$

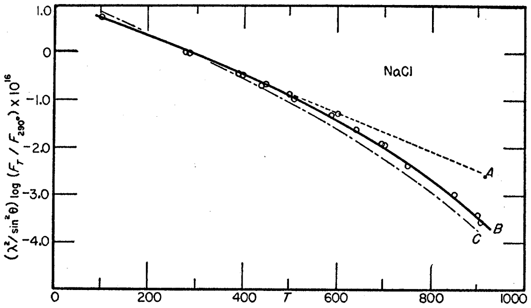

FIG. 1. Experimental points are marked by circles. Curve A, theoretical curve with constant Θ. Curves C and B, theoretical curves with Θ calculated by Eq. (5), with $\Theta(0)=281$, $\Theta(0)=298$, respectively.

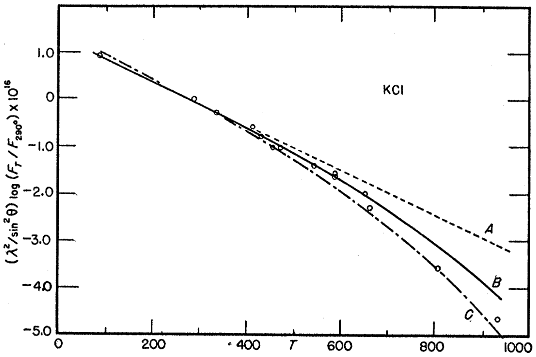

FIG. 2. Experimental points are marked by circles. Curve A, theoretical curve with constant Θ. Curves C and B, theoretical curves with Θ calculated by Eq. (5), with $\Theta(0)=230$, $\Theta(0)=240$, respectively.

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[9] Eucken, *Handbuch der Experimentalphysik*, Vol. VIII/1 (1929), p. 204.

[10] Courant and Hilbert, *Methoden der Mathematischen Physik* Vol. I (1924), pp. 2, 33.

TABLE III. The second row gives for various values of Poisson's ratio the ratio for an elastically isotropic solid of the Θ which must be used in the Debye factor, Eq. (1), for the intensity of x-ray reflection to the Θ which must be used in the Debye expression for the specific heat.

σ	0.25	0.3	0.35	0.4	0.45	0.5
Θ_μ/Θ_{C_V}	1.025	1.027	1.032	1.040	1.051	1.070

TABLE IV.

ELEMENT	TRANSITION TEMPERATURE (°K)	HEAT OF TRANSFORMATION (calories per gram atom)	$\frac{M_2}{M_1}$
Tin[1]	298	564	1.54
Arsenic[2]	1017	525	1.19
Selenium[3]	423	174	1.15
Zinc[4]	618	190	1.11
Manganese [5]	1108	158	1.05
	1317	249	1.06
Calcium[6]	673	100	1.05
Thallium[7]	498	51	1.03

[1] Lewis and Randel, *Thermodynamics* (1923), p. 464.
[2] Laschtschenko, J. Chem. Soc. **121**, 972 (1922).
[3] Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. X, p. 715.
[4] Reference 3, Vol. IV, p. 430.
[5] Umino Science Reports, Tohoku University **16**, 775 (1927).
[6] *International Critical Tables*, Vol. VII, p. 293.
[7] Werner, Zeits. f. anorg. Chemie **83**, 275 (1913).

where θ_t, θ_l refer to the characteristic temperatures associated with the transverse and longitudinal vibrations, respectively. The Θ defined by the second average, say Θ_μ, is given by

$$\Theta_\mu^{-2} = (2\theta_t^{-2} + \theta_l^{-2})/3.$$

The ratio Θ_μ/Θ_{C_V} will in this case be a function only of Poisson's ratio σ, and is given in Table III. The elastic anisotropy of all actual crystals will still further increase the ratio of the two types of average.

§3. RELATIONSHIP BETWEEN THE TEMPERATURE FACTORS OF ALLOTROPIC FORMS OF THE SAME ELEMENT

According to the Debye model of a solid, each crystal phase is associated with a definite characteristic temperature (which according to §2 must, however, be regarded as a function of temperature). The value of the characteristic temperature Θ_1 of the low temperature modification at the transition temperature T_0 may be calculated as described in §2. The value of the characteristic temperature Θ_2 of the high temperature modification at T_0 may at once be obtained from the entropy equation

$$S_D\{\Theta_2/T_0\} - S_D\{\Theta_1/T_0\} = L/T. \qquad (6)$$

Here L is the latent heat of the transition (in calories per gram atom when S is the entropy per gram atom). The solution of this equation for Θ_2 may be affected either by use of tables[12] of $S_D(\Theta/T)$ or, when $T > \Theta$, by the analytical expression[11] for S_D. When $T > 1.25\Theta$, the following equation gives S with an error of less than 1 percent:

$$S_D = R\{4 + 3 \ln T/\Theta\}.$$

Substitution of this equation into (6) gives

$$\Theta_1/\Theta_2 = e^{L/(3RT_0)}.$$

Using Eq. (1), we obtain

$$M_2/M_1 = e^{2L/(3RT_0)} \qquad (7)$$

for the ratio of the two M's at the transition temperature.

When a crystal phase is anisotropic, the Debye function M will vary with the orientation of the reflecting plane.[13] In this case Eq. (7) can only be valid when M_1 and M_2 refer to some sort of average. The correct type of average may be uniquely obtained when $T > \Theta$. In this case the Einstein model of a solid may be used to describe the vibrations of the atoms. In this model each atom is considered as bound elastically to a fixed lattice point. Let μ_{1x}, μ_{1y}, μ_{1z} and μ_{2x}, μ_{2y}, μ_{2z} be the mean squares of the displacement of the atoms along the three principal axes, for the low and high temperature phase, respectively. The change of entropy may then be written in terms of the ratio of two phase integrals.[14]

$$\frac{L}{T_0} = -R \ln \frac{\iiint_{-\infty}^{\infty} e^{-\frac{1}{2}(x^2/\mu_{1x} + y^2/\mu_{1y} + z^2/\mu_{1z})} dxdydz}{\iiint_{-\infty}^{\infty} e^{-\frac{1}{2}(x^2/\mu_{2x} + y^2/\mu_{2y} + z^2/\mu_{2z}} dxdydz}.$$

The reduction of this integral gives

$$\mu_{2x}\mu_{2y}\mu_{2z}/\mu_{1x}\mu_{1y}\mu_{1z} = e^{2L/RT_0}.$$

Using Eq. (2), we see that this equation is equivalent to Eq. (7) where now M stands for the geometrical mean $(M'\,M''\,M''')^{\frac{1}{3}}$. Here M', M'', M''' are the three M's in which the reflecting plane is normal to a principal axis. Table IV gives a list of the ratios M_2/M_1 which are predicted by Eq. (7).

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[11] An analytical expression for $S(x)$ is given by Gruniesen, *Handbuch der Physik*, Vol. X (1926), 22.

[12] Extensive tables of $S_D(x)$ are given by Simon, *Handbuch der Physik*, Vol. X (1926), pp. 369–370.

[13] Zener, Phys. Rev. **49**, 122 (1936).

[14] Herzfeld, *Kinetische Theorie der Warme* (1925), p. 161.