

the observed shift for Cr^{3+} (-2.8×10^{-10}) gives $dB/dp = -0.09 \text{ cm}^{-1}/\text{kbar}$ (for hydrostatic pressure), i.e., $l/B dB/dl \doteq +0.75$ (l is a unit cell dimension). The figure for V^{2+} is presumably about the same.

CONCLUSIONS

The experimental splittings agree so well with theory that one is tempted to conclude that the point charge model is valid for V^{2+} and Cr^{3+} ions in MgO , and that the Hartree-Fock wave function of the free ion is a good approximation to the wave function in the crystal. However, as pointed out in I, the model (using this wave function) gives quite the wrong value for the cubic field parameter Dq . Presumably this discrepancy is due to covalency effects,² which for some reason are not important, or cancel out, in the noncubic crystal field induced by strain. Furthermore, in the closely related case of $(3d)^3$ ions in Al_2O_3 , the model gives the wrong sign for the trigonal field parameter.^{3,4} This has been

explained by McClure³ as being due to a shift of the ion along the C_3 axis, but even so he has to assume a wave function substantially more extended than that of the free ion.¹⁰ Either Al_2O_3 is so much more covalent than MgO that the wave functions of a $(3d)^3$ ion are quite different in the two lattices, or the geometrical arrangement of ions in Al_2O_3 is substantially modified by the presence of the impurity. The similarity of the spectra in the two lattices inclines one to believe the latter alternative.

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¹⁰ However large a shift along the C_3 axis one permits, it appears to be impossible to obtain a trigonal field parameter of the correct sign using free ion wave functions (at any rate from the nearest neighbor potential).

Temperature Dependence of the Debye Temperatures for the Thermodynamic Functions of Alkali Halide Crystals*

M. P. TOSI AND F. G. FUMI†

Argonne National Laboratory, Argonne, Illinois

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The temperature dependence at constant volume of the experimental Debye temperatures for the entropy, the thermal energy, and the heat capacity at constant volume of potassium chloride, bromide and iodide, and of sodium iodide is analyzed over a wide range of temperature ($30^\circ\text{K} \lesssim T \lesssim 270^\circ\text{K}$) taking into account anharmonic effects. The inclusion of the leading anharmonic contribution into the quasiharmonic expansions of the Debye temperatures for the three thermodynamic functions allows one to reproduce over the entire temperature range the curves for the entropy, which are the most accurate, and also those for the thermal energy. The curves for the heat capacity are reproduced at the lower temperatures, and their proper course is indicated at the higher temperatures, where they are affected by sizeable uncertainties. The different form of the temperature dependence of the Debye temperatures for the three functions in the quasiharmonic temperature range, and the different magnitude of the effect of the anharmonic contributions on the Debye temperatures for the three functions at high temperature, are clearly illustrated. Refined values are obtained in each salt for the geometric mean of the vibrational frequencies and for the first few moments of the vibrational spectrum. The good agreement between the values of the moments derived from the three functions confirms the good validity of the quasiharmonic description of the thermal free energy at the lower temperatures. Values are obtained for the anharmonic contributions to the thermodynamic functions at high temperature.

1. INTRODUCTION

THE temperature dependence of a thermodynamic function of an insulator at constant pressure is commonly described by an appropriate Debye temperature, which is, in general, temperature-dependent. A preliminary report of this work has been given in Ref. 1. For a cubic insulator the observed temperature

dependence of a Debye temperature at constant pressure can be easily converted into the dependence at constant volume by correcting for the effect of thermal expansion. The temperature dependence of a Debye temperature at constant volume is in turn a quantity on which one can make some general theoretical predictions.² The expansion of the quasiharmonic expression for a thermodynamic function in inverse powers of the

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† Part time address: Department of Physics, Northwestern University, Evanston, Illinois.

¹ M. P. Tosi and F. G. Fumi, *Bull. Am. Phys. Soc.* **6**, 293 (1961).

² F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids* **23**, 395 (1962).

absolute temperature (Thirring-Stern expansions) leads one to anticipate that the temperature dependence of the Debye temperatures for different functions should be different in the range of moderate temperature. The Debye temperatures for the different functions should also approach different values in the limit of high temperature. In this limit, however, anharmonic contributions to the thermodynamic functions are expected to become relevant and one can anticipate that they will affect differently the temperature dependence of the different Debye temperatures.

We propose to discuss these expectations in detail and to show that they are borne out by experiment. To this end, we will give the quasiharmonic expansions for the Debye temperatures for the entropy, the thermal internal energy and the heat capacity at constant volume in inverse powers of the absolute temperature, and we will derive the leading anharmonic correction to these expansions. We will then use these formulas to analyze the observed temperature dependence at constant volume of the Debye temperatures for these thermodynamic functions in some potassium and sodium halides. The experimental Debye temperature for the entropy is most accurately known, and most easily obtained, at all temperatures, since the entropy is derived directly from the measured values of the heat capacity at constant pressure, without using thermodynamic corrections. We will see that the quasiharmonic analysis of the different thermodynamic functions at moderate temperature leads in each salt to the same values for the moments of the vibrational frequency spectrum, thus confirming the good validity of the quasiharmonic expression for the thermal free energy at these temperatures. We will see also that the analysis of the entropy at higher temperatures, including the leading anharmonic correction, permits one to obtain fairly accurate values for the anharmonic contribution. These are consistent with the data on the thermal energy and on the heat capacity at constant volume. A quasiharmonic analysis of the heat capacity at constant volume of the same salts at moderate temperature, based on the quasiharmonic expansion of the pertinent Debye temperature, had already been carried out by Barron, Berg, and Morrison.³ The value of such an expansion had been suggested earlier by Domb and Salter.⁴

2. THEORETICAL DISCUSSION

The quasiharmonic expressions of the thermodynamic functions of a cubic insulator reduce at moderate and high temperatures to the so-called Thirring-Stern expansions. For the entropy, the thermal energy and the heat capacity at constant volume these expansions

can be written as follows [Ref. 2, Eqs. (A2) to (A6)]:

$$\frac{S^h}{3Nk} = -\ln \frac{\Theta_0}{T} + \frac{4}{3} - \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{2n-1}{2n} \frac{3}{2n+3} \left(\frac{\Theta_{2n}}{T} \right)^{2n}, \quad (1)$$

$$\frac{W_{th}^h}{3NkT} = 1 - \frac{3}{8} \frac{\Theta_1}{T} - \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{3}{2n+3} \left(\frac{\Theta_{2n}}{T} \right)^{2n}, \quad (2)$$

$$\frac{C_V^h}{3Nk} = 1 + \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{3(2n-1)}{2n+3} \left(\frac{\Theta_{2n}}{T} \right)^{2n}, \quad (3)$$

where the B 's are the Bernoulli numbers. The characteristic temperatures Θ_n are related to the geometric mean of the vibrational frequencies and to the moments of the vibrational spectrum of the solid, and are purely volume-dependent functions. This particular version of the Thirring-Stern expansions has the feature that each expansion takes the form of the corresponding Debye expansion when the various characteristic temperatures Θ_n are replaced by an appropriate Debye temperature. This depends on temperature and volume. This correspondence suggests at once the possibility of obtaining expansions of the quasiharmonic Debye temperatures for the entropy, the thermal energy and the heat capacity in inverse powers of the absolute temperature.

The starting point of the derivation is the identification of the Debye expansion of a given thermodynamic function, containing a temperature-dependent Debye temperature, with the corresponding Thirring-Stern expansion. It is then immediately apparent that the expansions of the quasiharmonic Debye temperatures for the entropy and for the heat capacity contain only even powers of T^{-1} , and that the high-temperature limits of the quasiharmonic Debye temperatures for the entropy, the thermal energy and the heat capacity are Θ_0 , Θ_1 , and Θ_2 , respectively. The detailed derivation involves the introduction of the inverse-temperature expansion of the Debye temperature into the Debye expansion, the ordering of the terms in increasing powers of T^{-1} and the identification of the resulting coefficients with the corresponding coefficients of the Thirring-Stern expansion. The leading terms of the resulting expansions of the quasiharmonic Debye temperature for the entropy (Θ_S^h), for the thermal energy (Θ_W^h) and for the heat capacity (Θ_C^h) are as follows:

$$\Theta_S^h = \Theta_0 \left(1 + \sum_{n=1}^{\infty} a_n T^{-2n} \right);$$

$$a_1 = \frac{1}{40} (\Theta_0^2 - \Theta_2^2);$$

³ T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. A242, 478 (1957).

⁴ C. Domb and L. Salter, Phil. Mag. 43, 1083 (1952).

$$a_2 = \frac{1}{2240}(\Theta_4^4 - \Theta_0^4) + \frac{a_1}{2}(a_1 + \frac{1}{10}\Theta_0^2);$$

$$a_3 = \frac{1}{108864}(\Theta_0^6 - \Theta_6^6) + a_1(a_2 - \frac{1}{3}a_1^2) + \frac{\Theta_0^2}{40}\left(2a_2 + a_1^2 - \frac{\Theta_0^2}{14}a_1\right); \quad (4)$$

$$\Theta_w^h = \Theta_1 + \sum_{n=1}^{\infty} b_n T^{-n};$$

$$b_1 = \frac{2}{15}(\Theta_1^2 - \Theta_2^2); \quad b_2 = \frac{4}{15}\Theta_1 b_1;$$

$$b_3 = \frac{1}{630}(\Theta_4^4 - \Theta_1^4) + \frac{2}{15}(2\Theta_1 b_2 + b_1^2); \quad (5)$$

$$(\Theta_c^h)^2 = \Theta_2^2 + \sum_{n=1}^{\infty} c_n T^{-2n};$$

$$c_1 = \frac{1}{28}(\Theta_2^4 - \Theta_4^4); \quad c_2 = \frac{5}{4536}(\Theta_6^6 - \Theta_2^6) + \frac{\Theta_2^2}{14}c_1;$$

$$c_3 = \frac{1}{31680}(\Theta_2^8 - \Theta_8^8) + \frac{c_1^2}{28} + \frac{\Theta_2^2}{14}\left(c_2 - \frac{5}{108}\Theta_2^2 c_1\right). \quad (6)$$

These expansions can be expected to converge rapidly over the temperature range of convergence of the Thirring-Stern expansions. A noteworthy feature of the expansion of Θ_w^h is that the coefficients of the even powers of T^{-1} are completely determined by the coefficients of the previous terms of the expansion. The first three terms of the expansion of $(\Theta_c^h)^2$ had already been given by Barron *et al.*³

At temperatures where the anharmonic contributions to a thermodynamic function are not negligible, but still such that the function does not exceed the range of values of the corresponding Debye function, the appropriate Debye temperature will differ from the quasiharmonic Debye temperature by a correction factor. We determine this factor in the limit of moderately high temperatures where the vibrational free energy, inclusive of the anharmonic contributions deriving from cubic and quartic terms in the potential energy, has the form⁵

$$\frac{F_{\text{vib}}}{3Nk} = \frac{F_{\text{vib}}^h}{3Nk} - \frac{1}{2}AT^2 + B + O(T^{-2}). \quad (7)$$

Here A and B are purely volume-dependent functions.

⁵ See, for example, A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, *Ann. Phys. (N. Y.)* **15**, 337 (1961) [Eqs. (3.13) and (3.15)].

The quantity

$$AT = \frac{S - S^h}{3Nk} = \frac{W_{\text{th}} - W_{\text{th}}^h}{\frac{3}{2}NkT} = \frac{C_V - C_V^h}{3Nk} \quad (8)$$

gives, thus, the leading anharmonic contribution to the thermodynamic functions of interest⁶ and is, of course, subject to the restriction $|AT| < 1$.

The starting point of the derivation is again the identification of the Debye expansion of a given thermodynamic function with the corresponding Thirring-Stern expansion, corrected, however, by the leading anharmonic term. The cancellation of the quasiharmonic contribution from the two sides of the equation yields directly the following equations for the Debye temperature for the entropy (Θ_s), for the thermal energy (Θ_w) and for the heat capacity (Θ_c):

$$\ln \frac{\Theta_s}{\Theta_s^h} + \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{2n-1}{2n} \frac{3}{2n+3} \times \left(\frac{\Theta_s^h}{T}\right)^{2n} \left[\left(\frac{\Theta_s}{\Theta_s^h}\right)^{2n} - 1\right] = -AT, \quad (9)$$

$$\frac{3}{8} \frac{\Theta_w^h}{T} \left(\frac{\Theta_w}{\Theta_w^h} - 1\right) + \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{3}{2n+3} \times \left(\frac{\Theta_w^h}{T}\right)^{2n} \left[\left(\frac{\Theta_w}{\Theta_w^h}\right)^{2n} - 1\right] = -\frac{1}{2}AT, \quad (10)$$

$$\sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{3(2n-1)}{2n+3} \left(\frac{\Theta_c^h}{T}\right)^{2n} \left[\left(\frac{\Theta_c}{\Theta_c^h}\right)^{2n} - 1\right] = AT. \quad (11)$$

We write the ratio between each Debye temperature and the corresponding quasiharmonic Debye temperature as a power series in AT and determine the coefficients of the expansion by the type of procedure outlined above for the quasiharmonic expansions. The coefficients are found to decrease in magnitude as their order increases. The leading terms of the resulting expressions for the various Debye temperatures are as follows:

$$\Theta_s = \Theta_s^h \left[1 + AT / \left(\frac{\Theta_s^h}{T} \right) \frac{d}{d(\Theta_s^h/T)} \left(\frac{S^h}{3Nk} \right) \right], \quad (12)$$

$$\Theta_w = \Theta_w^h + \left[\frac{1}{2}AT^2 / \frac{d}{d(\Theta_w^h/T)} \left(\frac{W_{\text{th}}^h}{3NkT} \right) \right], \quad (13)$$

⁶ The thermal energy contains, in fact, also a purely volume-dependent anharmonic term. However, this does not need to be considered in the subsequent analysis since an analogous term is present also in the quasiharmonic thermal energy.

$$\Theta_c^2 = (\Theta_c^h)^2 + \left[AT^3 / \frac{d}{d(\Theta_c^h/T)^2} \left(\frac{C_V^h}{3Nk} \right) \right]. \quad (14)$$

A rough estimate of the deviations from unity of the ratios between each Debye temperature and the corresponding quasiharmonic Debye temperature indicates that the anharmonic contributions affect the Debye temperature for the entropy by a percentage comparable to their fractional weight in the heat capacity, and that the deviations for the three functions are approximately in the ratio $1:\frac{4}{3}(T/\Theta_1):10(T/\Theta_2)^2$ when $|AT| \ll 1$.

3. EXPERIMENTAL DATA

We consider four salts, namely, potassium chloride, bromide, and iodide and sodium iodide. The primary data for the construction of the curves for the temperature dependence at atmospheric pressure of the experimental Debye temperatures for the entropy, the thermal energy and the heat capacity at constant volume in these salts are the experimental values of the heat capacity at constant pressure. We have adopted the values measured by Berg and Morrison,⁷ which have an estimated accuracy of 0.2% at $T > 20^\circ\text{K}$. Appropriate numerical integrations of these data yield directly the entropy S and the thermal enthalpy H as functions of temperature at atmospheric pressure. The thermal energy W_{th} is derived from the enthalpy by means of the following relationships:

$$H(V, T) = W_{\text{th}}(V, T) + W_C(V) - W_C(V_0) + P(V - V_0) \quad (15)$$

and [Ref. 2, Eqs. (2) and (14)]

$$W_C(V) - W_C(V_0) \simeq -P(V - V_0) + (V - V_0)^2 / 2V_0K_0. \quad (16)$$

Here $W_C(V)$ is the cohesive energy of the solid of volume V at the absolute zero, and V_0 and K_0 are the volume and the isothermal compressibility of the solid at the absolute zero. Thus,

$$W_{\text{th}}(V, T) \simeq H(V, T) - (V - V_0)^2 / 2V_0K_0. \quad (17)$$

The heat capacity at constant volume is derived also from the heat capacity at constant pressure by means of the standard thermodynamic formula

$$C_V = C_P - (T\beta^2 V / K), \quad (18)$$

where β is the coefficient of volume thermal expansion.

The data necessary for these conversions are the density, the coefficient of volume thermal expansion and the isothermal compressibility as functions of temperature at atmospheric pressure. We have fitted the experimental values for the density at atmospheric

pressure reported by Henglein⁸ at three temperatures with the three-parameter formula⁹

$$\rho = \rho_0 [1 - \alpha T D_W(\Theta/T)], \quad (19)$$

where $D_W(\Theta/T)$ is the Debye function for the ratio between the thermal energy and $3NkT$. Equation (19) yields then the following expressions for β and K :

$$\beta = (\rho_0/\rho)\alpha D_C(\Theta/T), \quad (20)$$

$$K = K_0 - \frac{\rho_0}{\rho} T \left[\left(\frac{d\alpha}{dP} + \frac{\alpha^2 V_0}{3Nk} \right) D_W\left(\frac{\Theta}{T}\right) - \frac{\alpha^2 V_0}{3Nk} D_C\left(\frac{\Theta}{T}\right) \right], \quad (21)$$

where $D_C(\Theta/T)$ is the Debye function for the heat capacity at constant volume divided by $3Nk$. In the equation for K the quantity $(1/\Theta)d\Theta/dP$ has been eliminated by identifying the isothermal pressure derivative of the Debye function for the entropy with the corresponding derivative of the entropy of the solid. While the equation for β involves only the parameters entering ρ , the equation for K involves two additional parameters. The values adopted for the various parameters are reported in Table I. The

TABLE I. Empirical parameters for the density, the isothermal compressibility, and the thermal expansion.

	ρ_0 (g/cm ³)	α (10 ⁻⁴ deg ⁻¹)	Θ (°K)	K_0 (10 ⁻¹² cm ² /dyn)	$d\alpha/dP$ (10 ⁻¹⁵ cm ² /dyn deg)	γ
KCl	2.0336	1.06	252.0	4.88	-3.82	1.5
KBr	2.8204	1.13	208.3	5.70	-4.52	1.6
KI	3.2128	1.27	177.5	7.08	-5.57	1.7
NaI	3.7640	1.38	210.5	6.19	-1.49	1.7

expression for β reproduces well the experimental values in potassium chloride^{10,11} in the temperature range from 50 to 200°K. At temperatures below 50°K the computed value becomes significantly larger than the measured value but in this range the correction $C_P - C_V$ is quite unimportant. At temperatures $T \simeq \Theta_2$ the measured value exceeds the computed value by about 3% and the discrepancy increases rapidly with increasing temperature.¹² This effect is apparent also

⁸ F. A. Henglein, Z. Phys. Chem. **115**, 91 (1925).

⁹ See, for example, G. Leibfried and O. Hahn, Z. Physik **150**, 497 (1958).

¹⁰ T. Rubin, H. L. Johnston, and H. W. Altman, J. Phys. Chem. **66**, 948 (1962).

¹¹ G. K. White, Phil. Mag. **6**, 1425 (1961); D. E. Schuele, AEC Tech. Rept. No. 23 Contract AT(11-1)-623, 1962.

¹² A fit of Henglein's values for the density of sodium chloride by Eq. (19) leads to analogous discrepancies from the values of β measured by Rubin *et al.* [T. Rubin, H. L. Johnston, and H. W. Altman, J. Phys. Chem. **65**, 65 (1961)].

⁷ W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 467 (1957). We are indebted to the Royal Society of London for sending us a copy of the complete tables of the primary results.

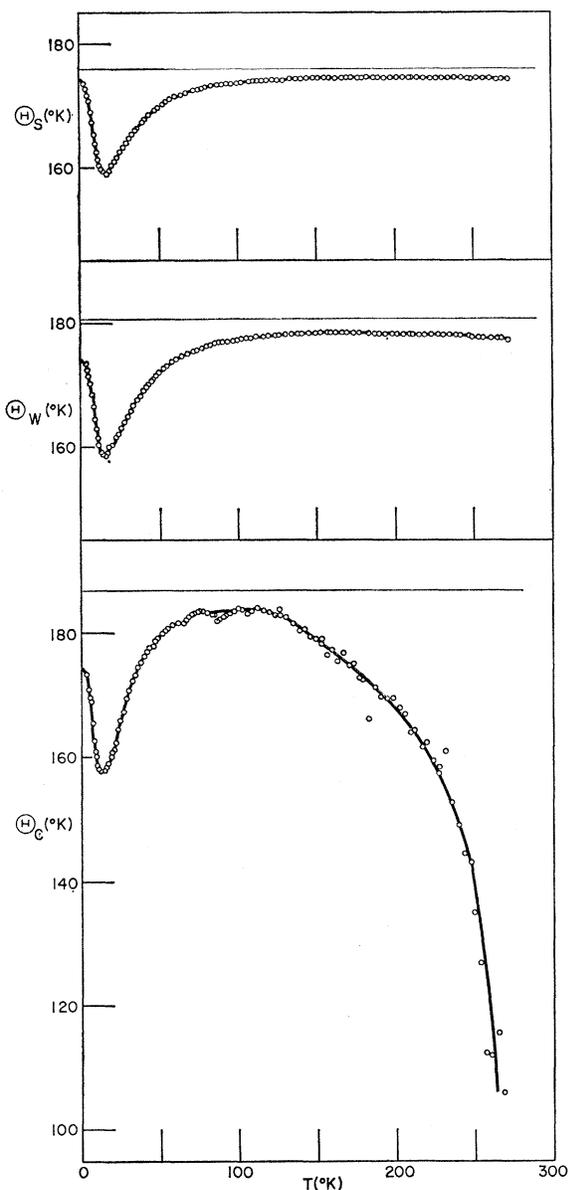


FIG. 1. Temperature dependence of the experimental Debye temperatures (referred to the volume at 0°K) for the entropy, the thermal energy, and the heat capacity at constant volume in KBr. The horizontal lines denote the quasi-harmonic limits of the Debye temperatures for the different functions at high temperature.

in potassium bromide¹³ possibly with a larger magnitude. The expression for K fits closely the data of Galt¹⁴ for potassium bromide over the whole temperature range. It fits also the data of Durand¹⁵ and of Norwood and Briscoe¹⁶ for potassium chloride within their

¹³ D. Bijl, *Conférence de physique des basses températures*, Suppl. Bull. Inst. Int. Froid (Paris), 445 (1955).

¹⁴ J. K. Galt, *Phys. Rev.* **73**, 1460 (1948).

¹⁵ M. A. Durand, *Phys. Rev.* **50**, 449 (1936).

¹⁶ M. H. Norwood and C. V. Briscoe, *Phys. Rev.* **112**, 45 (1958).

discrepancy of a few percent. In potassium and sodium iodide the expression fits the data of Spangenberg¹⁷ and of Bridgman,¹⁸ and its deviation from the data of Norwood and Briscoe¹⁶ and of Claytor and Marshall¹⁹ reaches 10% only at low temperature. Data pertaining

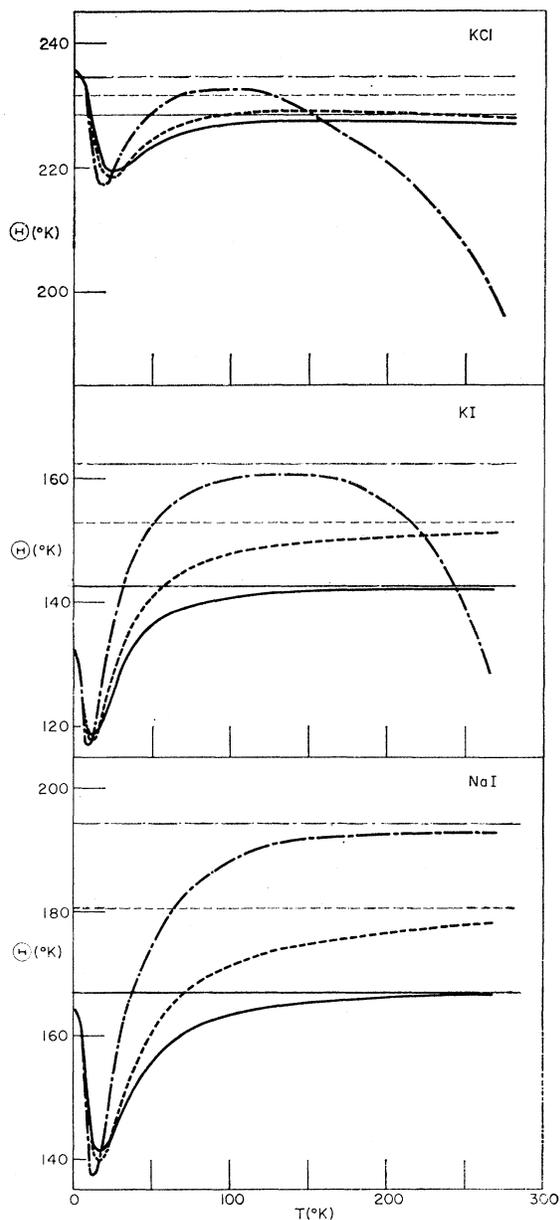


FIG. 2. Temperature dependence of the experimental Debye temperatures (referred to the volume at 0°K) for the entropy (solid curves), the thermal energy (dashed curves), and the heat capacity at constant volume (dot-dash curves) in KCl, KI, and NaI. The horizontal lines denote the quasi-harmonic limits of the Debye temperatures for the different functions at high temperature.

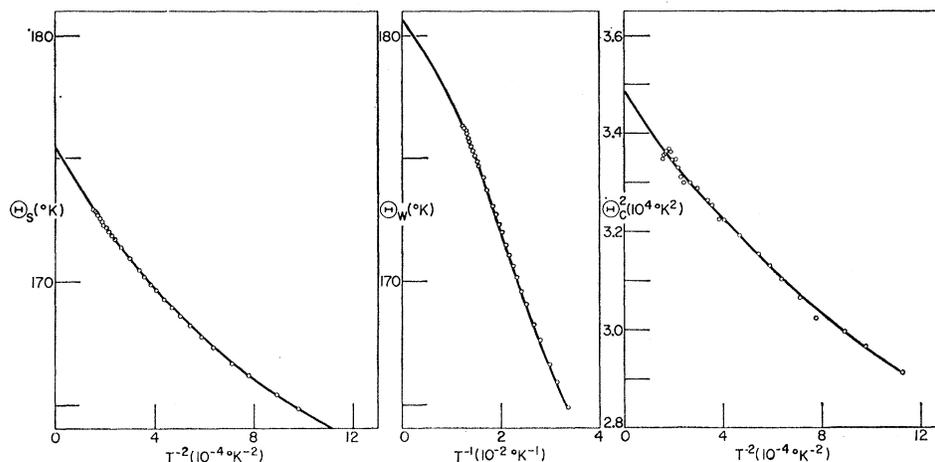
¹⁷ K. Spangenberg, *Naturwiss.* **43**, 394 (1956).

¹⁸ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **74**, 21 (1940).

¹⁹ R. N. Claytor and B. J. Marshall, *Phys. Rev.* **120**, 332 (1960).

FIG. 3. Quasi-harmonic fit of the experimental Debye temperatures (referred to the volume at 0°K) for the entropy, the thermal energy, and the heat capacity at constant volume in KBr in the temperature range $\frac{1}{6}\Theta_D \leq T \leq 80^\circ\text{K}$.

The leading term of the inverse-temperature expansion of each Debye temperature is given by the intercept on the ordinate axis.



to the adiabatic compressibility were, of course, converted into the isothermal compressibility by the standard thermodynamic formula.

Figures 1 and 2 give the plots of the experimental Debye temperatures for the entropy, the thermal energy, and the heat capacity as functions of temperature at constant volume for the four salts in question. The constant volume was taken equal to the volume at 0°K. The experimental Debye temperatures at atmospheric pressure were corrected for thermal expansion by the approximate formula³

$$\Theta(V_0, T)/\Theta(V, T) = (\rho_0/\rho)^\gamma,$$

where γ is an appropriate Grüneisen parameter. This was taken as a constant in each salt,³ and was computed by the Grüneisen formula at temperatures somewhat below room temperature using the expressions given above for ρ , β , and K . The values adopted for γ are reported in Table I. The values for potassium chloride and bromide agree with the experimental values of the Grüneisen parameter at moderate and high temperatures reported by White and Schuele¹¹ and by Bijl¹³ within about 3%.

A cursory examination of Fig. 1 reveals that the scatter of the experimental points in the plots of the experimental Debye temperature for the heat capacity is largely eliminated by the integration in the plots for the entropy and for the thermal energy. The accuracy of all the plots is affected, in principle, by the approximate correction for the thermal expansion. However, at low temperatures, this correction is quite small and in the region between 200 and 270°K, where it reaches a few percent, it should be rather accurate, especially for the entropy. In fact, within the quasi-harmonic approximation, the high-temperature limit of the Grüneisen γ is identical to the logarithmic volume derivative of the Debye characteristic temperature for the entropy at high temperature.²⁰ The plots for the entropy are thus expected to be quite accurate. The

plots for the thermal energy and for the heat capacity involve additional corrections and are affected by the uncertainties in the pertinent data. However, an uncertainty of 10% in the correction $(V - V_0)^2/2V_0K_0$ causes an uncertainty in the Debye temperature for the thermal energy which reaches only 0.3% at temperatures of the order of the Debye temperature. For the heat capacity, instead, an underestimate of only 3% in β at temperatures of the order of the Debye temperature implies already an underestimate of the Debye temperature of over 2%. At higher temperatures, the underestimate in β increases rapidly, and so does the effect of the $C_P - C_V$ correction on the Debye temperature. This renders the plots for the heat capacity of little meaning at high temperature.

4. ANALYSIS OF THE DATA

In this section we apply the theoretical results of Sec. 2 to analyze the plots obtained in Sec. 3 for the temperature dependence at constant volume of the experimental Debye temperatures for the entropy, the thermal energy, and the heat capacity at constant volume in potassium chloride, bromide, and iodide and in sodium iodide.

In the temperature region $\Theta_D/6 \leq T \leq 80^\circ\text{K}$ where Barron *et al.*³ had successfully performed a quasi-harmonic analysis for the heat capacity, we have used the quasi-harmonic expansions for the Debye temperatures. Specifically, we have carried out a least-squares fit of these expansions to the experimental Debye temperatures at constant volume, testing also the effect of small changes in the width of the temperature range and the effect of varying the number of terms retained in the expansions. While the first effect was found to be negligible, small variations in the values of the first few coefficients of each expansion were found in several cases when the number of terms was varied from a minimum of five to a maximum of eight. The values of the coefficients were also checked by graphical methods, analogous to those used by Barron *et al.*³ for

²⁰ T. H. K. Barron, *Phil. Mag.* **46**, 720 (1955).

TABLE II. Characteristic temperatures $\theta_n(V_0)$ ($^{\circ}\text{K}$).^a

	KCl			KBr			KI			NaI		
	<i>S</i>	<i>W</i> _{th}	<i>C_V</i>									
Θ_0	228.5±0.5	175.4±0.5	142.8±0.5	167.1±0.5
Θ_1	...	231.6±1.3	180.7±0.7	152.8±0.7	180.6±0.7	...
Θ_2	235.1±1.4	234.4±5 234.1±6	234.7±1.3	186.1±1.0	186.0±5 186.9±11	186.8±0.8	161.9±1.3	161.9±4 160.9±8	162.4±1.0	195.0±1.2	195.3±2 194.1±6	194.3±1.1
Θ_4	240.4±3	...	240.1±4	192.4±3	...	195.8±3	175.0±3	...	176.7±3	218.5±4	...	217.9±4
Θ_6	244.6±5	...	245.9±7	204.1±6	186.7±5	235.7±5
Θ_8	251.9±9	211.7±8

^a The two values of Θ_2 derived from the thermal energy are obtained from the coefficients of T^{-1} and of T^{-2} in the expansion of $\Theta_{\mathcal{W}^h}$.

the heat capacity. Figure 3 reports some of the pertinent graphs for potassium bromide. These illustrate quite clearly the different functional dependence on temperature at constant volume of the experimental Debye temperatures for the different functions.

Table II gives the values of the characteristic temperatures $\Theta_n(V_0)$ derived from the values of the first few coefficients in the expansions for the three thermodynamic functions, and their estimated probable errors. The probable error includes the effect of the uncertainty in the primary data and the effect of the change in the number of terms retained in the expansions. A significant feature of Table II is the good agreement between the values of each characteristic temperature in a given salt derived from the three thermodynamic functions. The values given in Table II agree also with the values reported by Barron *et al.*,³ who determined Θ_2 , Θ_4 , and Θ_6 from the heat capacity and used these values to calculate Θ_0 from the value of the entropy at 270°K and Θ_1 by interpolation. The values of the geometric mean of the vibrational frequencies and of the first few moments of the frequency spectrum, referred to the volume at 0°K, follow at once from the values of the characteristic temperatures.

Figures 1 and 2 show quite clearly that, in most cases, the experimental Debye temperatures for the three thermodynamic functions do not approach their quasi-harmonic limits at high temperatures. It is also apparent that the magnitude of the deviation increases in each salt as one passes from the entropy to the thermal energy and to the heat capacity. This suggests at once the role of the anharmonic contributions, in harmony with the comment made in Sec. 2 on the relative magnitude of their effect on the Debye temperatures for the different functions. Barron *et al.*³ implied, in fact, that the large deviation for the heat capacity is due entirely to the anharmonic contributions.

To attempt a quantitative analysis of the anharmonic effects, we have chosen to rely on the entropy since the experimental Debye temperatures for this function are the most accurate. In a first approximation, the anharmonic coefficient $A(V_0)$ was determined by means of Eq. (12) from the magnitude of the deviations between the experimental Debye temperature for the entropy at $T \gtrsim \Theta_2$ and the quasi-harmonic Debye

temperature computed with the values of the $\Theta_n(V_0)$'s reported in Table II. The resulting values of $A(V_0)$ were then corrected in an approximate fashion for the systematic error caused by the neglect of the anharmonic term in the fit of the entropy at low temperatures. The magnitude of $A(V_0)$ increases by more than 50% but the corrected values of the $\Theta_n(V_0)$'s agree with the previous values within their probable error. Table III

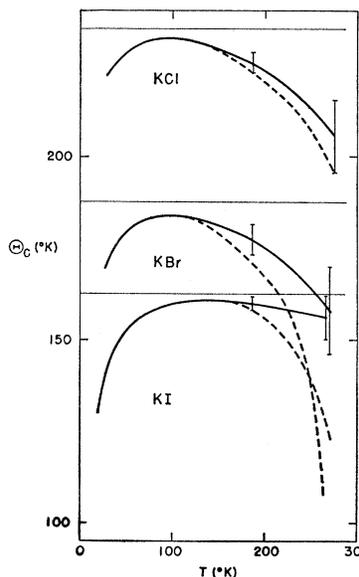
TABLE III. Anharmonic coefficient $A(V_0)$ (10^{-6} deg^{-1}).

KCl	KBr	KI	NaI
3±1	2.5±1	0.5±0.5	-0.2±0.5

reports the final values of $A(V_0)$ together with their estimated probable errors. These include the magnitude of the correction to $A(V_0)$ and the effect of the probable errors in the $\Theta_n(V_0)$'s.

The value of $A(V_0)$ derived from the entropy and the values of the $\Theta_n(V_0)$'s derived from the quasi-harmonic analysis of the thermal energy and of the heat capacity (slightly corrected to take account of the neglect of the anharmonic term in the low-temperature fits) have then been used to compute the Debye temperatures for these last two functions down to moderate temperatures by means of Eqs. (13) and (14). The agreement between the computed and the experimental Debye temperature for the thermal energy is found to be well within the precision of the computed value, which amounts to a couple of degrees. This provides a confirmation of the values of $A(V_0)$ derived from the entropy since the experimental Debye temperature for the thermal energy is expected to be fairly accurate. The computed Debye temperatures for the heat capacity with their uncertainties, determined mainly by the uncertainty in $A(V_0)$, are reported in Fig. 4 for the potassium halides. Here the discrepancy between the computed and the experimental values at high temperature is clearly outside the precision of the computed curve for potassium bromide and iodide, and is at the limit of this precision for potassium chloride. This discrepancy is consistent, however, in sign and in magnitude with the anticipated underesti-

FIG. 4. Temperature dependence of the Debye temperature (referred to the volume at 0°K) for the heat capacity at constant volume in the potassium halides at moderate and high temperatures. The solid curves are computed by means of Eq. (14) while the dashed curves are taken from Figs. 1 and 2.



mate of the experimental Debye temperature at high temperature, caused by the underestimate of the coefficient of thermal expansion. In fact, the use of the recently measured values for the coefficient of thermal expansion of potassium chloride¹⁰ in the $C_P - C_V$ correction leads to experimental Debye temperatures in good agreement with the computed values at high temperature.

5. DISCUSSION OF THE RESULTS

Our analysis shows that the temperature dependence at constant volume of the experimental Debye temperatures for the entropy and for the thermal energy of the four salts in question, which is determined quite accurately from the C_P data, is well reproduced over a wide range of temperature ($\frac{1}{8}\Theta_D \lesssim T \lesssim \frac{3}{2}\Theta_D$) by correcting the quasiharmonic expansions for the Debye temperatures for the effect of the leading anharmonic contribution. For the heat capacity at constant volume, instead, the computed and the experimental temperature dependence of the Debye temperature at constant volume deviate significantly at high temperature where the experimental Debye temperature is quite inaccurate. This underlines the advantage of basing the investigation of the anharmonic effects on the entropy.

The quasiharmonic analysis of the three thermodynamic functions at the lower temperatures displays clearly the different temperature dependence of the pertinent Debye temperatures. It yields also consistent values for the first few moments of the vibrational

spectrum, thus confirming the good validity of the quasiharmonic expression in describing the thermal free energy at these temperatures. Barron and Klein²¹ have recently proved analytically that the thermal free energy, inclusive of the anharmonic contributions arising from cubic and quartic terms in the potential energy, has in fact the quasiharmonic form at sufficiently low temperature, but involves a vibrational spectrum shifted relative to the spectrum of the quasiharmonic crystal.

The anharmonic analysis at the higher temperatures emphasizes the different magnitude of the effect of the anharmonic contributions on the Debye temperatures for the three functions, and yields, for the first time, experimental values for these anharmonic contributions at high temperature. The analysis indicates also that in the crystals in question the shift of the vibrational spectrum discussed by Barron and Klein²¹ affects the moments of the spectrum only by amounts comparable to the probable errors in the values derived from the quasiharmonic analysis.

The over-all agreement between the calculated vibrational spectra of the salts in question and the values of the moments derived from the quasiharmonic analysis of the thermal thermodynamic functions has recently been discussed thoroughly by Karo and Hardy.²² On the other hand, a comparison between the anharmonic contributions to the heat capacity at constant volume estimated by Leibfried and Ludwig²³ with a semiempirical model, and the values that we obtain from the analysis of the thermal thermodynamic functions, reveals that the former are consistently much too large. The discrepancy ranges from a factor of four in potassium chloride and bromide, to more than an order of magnitude in potassium and sodium iodide.

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²¹ T. H. K. Barron and M. L. Klein, *Phys. Rev.* **127**, 1997 (1962).

²² A. M. Karo and J. R. Hardy, *Phys. Rev.* **129**, 2024 (1963).

²³ G. Leibfried and W. Ludwig, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275 [Eq. (17.1) and Table XV].