Interpretation of Debye-Waller Factors

J. L. FELDMAN AND G. K. HORTON

Department of Physics, Rutgers University, New Brunswick, New Jersey

(Received 24 May 1963)

$\Theta^{DW}(T)$, calculated in the quasiharmonic approximation from thermodynamic data, is compared with the results of the Mössbauer experiment on tin of Boyle et al.; the difference between the curves increases with temperature and is significant. Boyle et al. interpreted their results as showing substantial anharmonic effects and suggested that this interpretation was reasonable by appealing to a model involving a single particle in a one-dimensional well. We have applied their model to a number of other elements, especially copper, germanium and silicon, and find that the Debye-Waller data are consistent with the calorimetric data only for tin. We conclude that the very simplified model of Boyle et al. may be unreliable. The Mössbauer results of Wiedemann et al. and Yaqub and Hohenemser are considered. In view of the reliability of calorimetric data and the experimental difficulties involved in making Mössbauer measurements it is felt that Wiedemann's value of 153°K for Θ_0^{DW} is too high by about 7%. The results of Yaqub and Hohenemser agree quite well with ours. They have apparently observed no evidence of vibrational anharmonicity in tin even at their highest temperature reading of 373°K.

I. INTRODUCTION

THE temperature dependence of the Debye-Waller factor for polycrystalline white tin has been determined by resonance experiments on the 24-keV line in Sn^{119}. Boyle et al.[1] have investigated the line in Sn^{119}. They have investigated the moderate- and high-temperature regions ($120°K \leq T \leq 500°K$) by "relative motion" (of absorber and source) techniques. Subsequently, Wiedemann et al.[2] and Yaqub and Hohenemser[3] have taken several measurements in the vicinity of the critical temperature, $T_c = 3.72°K$, using "relative motion" techniques and self-absorption techniques, respectively. Yaqub and Hohenemser have also taken measurements at moderate and high temperatures ($60°K \leq Y \leq 373°K$). In this paper we shall concern ourselves mainly with the results and interpretation of Boyle et al. and briefly comment on subsequent experiments in Sec. V.

In the Debye approximation the exponent $2W$ in the Debye-Waller factor is proportional to

$$X_D(T) = \int_0^{k\Theta_D/\hbar} \left(\tfrac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right) \left[\frac{G_D(\omega)}{\omega^2} \right] d\omega, \quad (1)$$

where $G_D(\omega)$ is the Debye frequency distribution and Θ_D is the characteristic temperature. As usual, we define an effective characteristic temperature $\Theta^{DW}(T)$ by replacing $X_D(T)$ in (1) by the experimental value and calculating the corresponding theta. $\Theta^{DW}(T)$ thus obtained from the data of Boyle et al. is found to decrease markedly with increasing temperature, even at moderate temperatures. Boyle et al. have interpreted their results in terms of anharmonicity of the lattice vibrations. Their interpretation is based on a single particle in a one-dimensional well and depends considerably on the quantitative predictions of this model.

It seemed surprising that marked vibrational anharmonicity in the Debye-Waller factor should be observed at moderate temperatures. A quantitative description of the experimentally measured anharmonicity of the lattice vibrations is obtained by subtracting the quasi-harmonic contribution from the data. Boyle et al. have estimated this contribution by choosing $\Theta^{DW}(V_0)$ as some unspecified average of low-temperature values of Θ^c (the calorimetric characteristic temperature) and by using an approximation due to Zener and Bilinsky[4] for the effects of volume dilation. V_0 is the volume at $T = 0$. In fact, the harmonic and quasiharmonic contributions to the Debye-Waller factor are clearly specified in terms of thermodynamic quantities. This result has also been stressed by Barron[5] et al. Since thermal data are quite reliable, the use of curve-fitting techniques can be avoided for substances whose thermodynamic properties are known.

II. THEORY

A. Constant Volume

We start with

$$X_{\text{harm}}(T) = \int_0^{\omega_{\max}} \left(\tfrac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right) \left[\frac{G(\omega)}{\omega^2} \right] d\omega, \quad (2)$$

where $G(\omega)$ is the frequency distribution. Strictly speaking, Eq. (2) is relevant only to single cubic crystals. However, as a first approximation, we shall apply it to polycrystalline tetragonal tin, which was used by Boyle et al., and we shall study directional effects in a separate paper.

By standard methods[6] one can show that in the

[1] A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, Proc. Phys. Soc. (London) **77**, 129 (1961).
[2] W. H. Wiedemann, P. Kienle, and F. Pobell, Z. Physik **166**, 109 (1962).
[3] M. Yaqub and C. Hohenemser, Phys. Rev. **127**, 2028 (1962).

[4] C. Zener and S. Bilinsky, Phys. Rev. **50**, 101 (1936).
[5] T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1962), p. 323.
[6] H. Thirring, Z. Physik **14**, 867 (1913).

FIG. 1. $\omega_D(n)$ for white tin. The solid circles represent our calculations from the thermal data. The triangle and square correspond to $\omega_D(-3)$ obtained from the determination of $\Theta_0{}^{el}=201.6°K$ by Rayne and Chandrasekhar and the determination of $\Theta_0{}^c=196.5°K$ by Gayley et al., respectively.
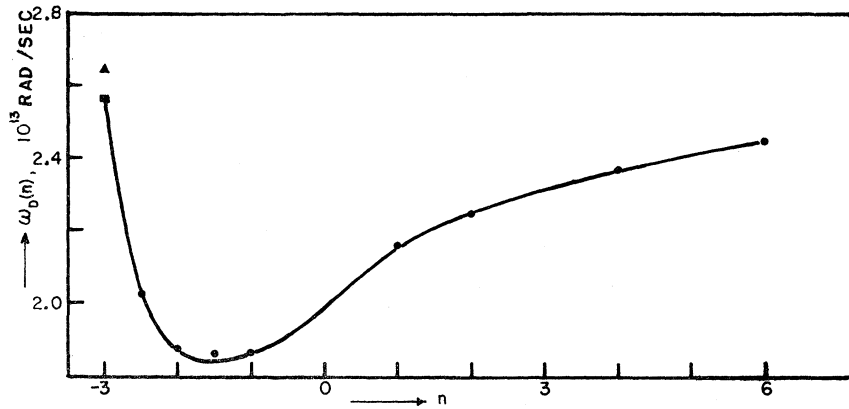
harmonic approximation $\Theta^{DW}(T)$ approaches

$$\Theta_h{}^{DW}=\Theta_\infty{}^{DW}\{1+(1/7200)[(\Theta_\infty{}^c/\Theta_\infty{}^{DW})^2-1]$$
$$\times(\Theta_\infty{}^{DW}/T)^4\cdots\}, \quad \text{for} \quad T\geq0.25\Theta, \quad (3)$$

and

$$\Theta_h{}^{DW}=\Theta_0{}^{DW}\{1+6.580[1-(\Theta_0{}^{DW}/\Theta_0{}^c)^3]$$
$$\times(T/\Theta_0{}^{DW})^2\cdots\}, \quad \text{for} \quad T\leq0.04\Theta, \quad (4)$$

where

$$\Theta_0{}^{DW}=\hbar\omega_D(-1)/k, \quad \Theta_0{}^c=\hbar\omega_D(-3)/k,$$
$$\Theta_\infty{}^{DW}=\hbar\omega_D(-2)/k, \quad \Theta_\infty{}^c=\hbar\omega_D(2)/k,$$

and

$$\omega_D(n)=[\langle\omega^n\rangle_{av}(n+3)/3]^{1/n}.$$

The moments appearing in Eqs. (3) and (4) can be calculated from calorimetric data[7] once the electronic specific heat, volume effects,[8] and vibrational anharmonicity[7] have been allowed for.

B. Constant Pressure

In the quasiharmonic approximation, volume expansion is accounted for by considering the volume dependence of $G(\omega)$ or equivalently, $\omega_D(n)$. Since dilation is appreciable only at moderate and high temperatures we consider the volume dependence in Eq. (3) only. Writing $V_T=V_0+\Delta V$, where V_0 is the volume at $T=0$, we obtain to first order in small quantities

$$\Theta_{qh}{}^{DW}=\Theta_\infty{}^{DW}(V_0)[1+\epsilon(T,V_0)$$
$$-\tilde\gamma(-2)\Delta V/V\cdots], \quad (5)$$

where

$$\epsilon(T,V_T)\equiv(1/7200)\{[\Theta_\infty{}^c(V_T)/\Theta_\infty{}^{DW}(V_T)]^2-1\}$$
$$\times[\Theta_\infty{}^{DW}(V_T)/T]^4,$$

and

$$\tilde\gamma(n)=-d\ln\omega_D(n)/d\ln V.$$

It can be shown, therefore, that the effect of volume dilation on the Debye-Waller factor depends on the

thermodynamic quantity, $\gamma(T)=\beta V/\kappa_s C_p$, through

$$\tilde\gamma(-2)=\int_0^\infty \gamma(T)\left(\frac{C_v{}^{harm}}{T^3}\right)dT \Big/ \int_0^\infty \left(\frac{C_v{}^{harm}}{T^3}\right)dT, \quad (6)$$

where β is the volume expansivity and κ_s the adiabatic compressibility.

To clarify the notation we point out that $\gamma(T)$ is the usual Grüneisen parameter. Later in this paper we will be particularly concerned with its value at $T=0$ which we have denoted by γ_0, i.e., $\gamma_0\equiv\gamma(0)$. In addition, following Barron,[9] it is useful to introduce related quantities, $\tilde\gamma(n)$ for $-3<n<0$, which do not depend on the temperature but represent temperature averages of the Grüneisen parameter, $\tilde\gamma(T)$. As an example $\tilde\gamma(-2)$ is given by (6).

III. THERMODYNAMIC DATA

The pertinent thermodynamic data and related information are listed in Table I.[10–14]

TABLE I. Thermodynamic data and related information.

Quantity	Type of measurement	Temp. range (°K)	Source of data
$C_p{}^a$	calorimetric	$0\leq T\leq300$	NBS (Ref. 10)
β	macroscopic	$68\leq T\leq282$	Erfling (Ref. 11)
Lattice constants	x ray	$T=4.2$	Rayne and Chandrasekhar (Ref. 12)
	x ray	$303\leq T\leq424$	Deshpande and Sirdeshmukh (Ref. 13)
Elastic constants	velocity calorimetric	$0<T\leq300$	Rayne and Chandrasekhar (Ref. 12)
Θ_0		$T\approx0$	Gayley et al. (Ref. 14)

a For $T\leq120°K$, C_v was obtained as usual from C_p measurements. The compressibility was determined as a function of temperature from elastic constant data.

[9] T. H. K. Barron, Phil. Mag. 46, 720 (1955).
[10] Natl. Bur. Std. (U.S.), Monograph 21, 13 (1960).
[11] H. D. Erfling, Ann. Physik 34, 136 (1939).
[12] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. 120, 1658 (1960).
[13] V. T. Deshpande and D. B. Sirdeshmukh, Acta Cryst. 14, 355 (1961).
[14] R. I. Gayley, Jr., E. A. Lynton, and B. Serin, Phys. Rev. 126, 43 (1962).

[7] T. H. K. Barron, W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 478 (1957).
[8] G. K. Horton, Proc. Roy. Soc. (London) A252, 551 (1959).

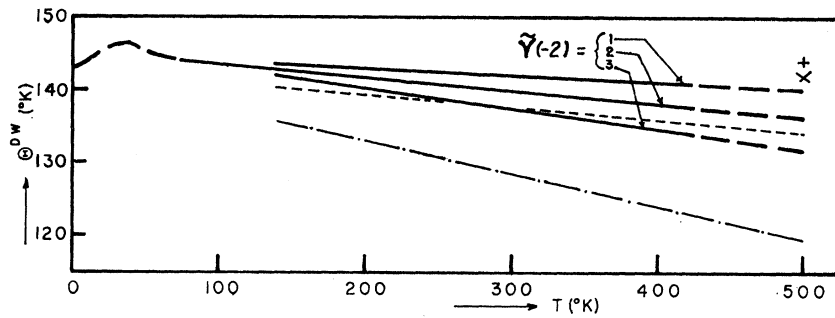FIG. 2. Θ^{DW} for white tin. The + and × represent $\Theta_h^{DW} = 144°K$ $(T \geq 60°K)$ calculated from the thermal data and $\Theta(V_0) = 142°K$ obtained by Boyle *et al.*, respectively. The heavy lines correspond to our calculation and estimated uncertainty of Θ_{qh}^{DW}, and the light dashed line to $\Theta(V_T)$ of Boyle *et al.* The partially dotted line was obtained from the experimental points of Boyle *et al.* (The heavy dashed line represents extrapolation.)

IV. RESULTS

The results of the moment calculations are shown in Fig. 1 in terms of an $\omega_D(n)$ plot. As in copper[5] $\omega_D(-1)$ and $\omega_D(-2)$ lie near the minimum of the curve thus indicating a nearly constant Θ_h^{DW}. There has been some disagreement over the calorimetric determination of Θ_0^c [or $\omega_D(-3)$]. We have simply plotted the most recent elastic constant[12] and calorimetric[14] determinations.

In Fig. 2, our results for Θ_h^{DW} snd Θ_{qh}^{DW} are compared with those of Boyle *et al.* The limiting values of our Θ_{qh}^{DW} are given by our estimate of the uncertainty of $\gamma(T)$ and hence $\bar{\gamma}(-2)$. Since C_v^h/T^3 is found to be rather sharply peaked at $T = 10°K$ it follows that low-temperature values of $\gamma(T)$ contribute predominantly to $\gamma(-2)$. Above $T = 68°K$, $\gamma(T)$ is approximately 2. However, $\gamma(T)$ below $68°K$ has not been measured, so we have invoked Grüneisen's Law to extrapolate $\gamma(T)$ to low temperatures and thus obtained $\gamma(-2) = 2.0$. The upper and lower lines correspond to our estimate of the likely variation of $\gamma(T)$ below $68°K$. We have shown in the Appendix how γ_0 can be found from the *temperature* dependence of the elastic constants. The available data for tin are unfortunately not detailed enough.

V. DISCUSSION

It is apparent from Fig. 2 that the predictions of the thermal data agree quite well with the predictions of Boyle *et al.* on the harmonic and quasiharmonic contributions to the Debye-Waller factor, and hence that their experimental results cannot be explained on the basis of quasiharmonic effects alone.

According to the *one-dimensional* model presented by Boyle *et al.* to explain their results, the specific heat and Debye-Waller exponent are given by

$$C_v = k\{1 + (kT/a)[15(b/a)^2 - 6(c/a)] \cdots\}, \quad (7)$$

and

$$2W \propto \langle x^2 \rangle_{av} = (kT/a)$$
$$\times \{1 + (kT/a)[45(b/a)^2 - 12(c/a)] \cdots\}, \quad (8)$$

where $\langle x^2 \rangle_{av}$ is the mean-square displacement and $\tfrac{1}{2}a$, b, and c are defined as the coefficients appearing in the potential. We have attempted to apply this model to

other substances, where both C_v and $2W$ are known at high T.

Equations (7) and (8) yield

$$\Delta C_v/C_v = (kT/a)[15(b/a)^2 - 6(c/a)] \cdots, \quad (9)$$

and

$$\Delta 2W/2W = (kT/a)[45(b/a)^2 - 12(c/a)] \cdots, \quad (10)$$

where ΔC_v and $\Delta 2W$ represent the anharmonic contribution to the specific heat and Debye-Waller exponent, respectively. Since $a > 0$ one obtains

$$\Delta 2W/2W > 2\Delta C_v/C_v. \quad (11)$$

Hence, if we believe the one-dimensional model of Boyle *et al.*, since $|\Delta C_v/C_v| \ll 1$ for copper[15] (so that $5b^2 \sim 2ac$) it is hard to see why $\Delta 2W/2W$ should also be negligible.[5] In germanium and silicon,[16] as in the case of tin,[10-12] where the anharmonic term in C_v is found to be positive, one would also expect to see large positive contributions to $2W$. The experimental results,[17] however, do not indicate any such effect. One must, therefore, conclude that the one-dimensional model cannot describe the experimental situation adequately.

The low-temperature results of Wiedemann *et al.*[2] indicate a Θ_0^{DW} of 153°K which disagrees with our low-temperature value of 143°K by 7%. In view of the reliability of calorimetric data involved in obtaining Θ_0^{DW} and the experimental difficulties involved in making Mössbauer measurements, but subject to modification by directional effects, we believe that the value of Wiedemann *et al.* is about 10°K too high.

The results of Yaqub and Hohenemser[3] can be fitted quite closely at all temperatures by a curve corresponding to $\Theta_0^{DW} = 140°K$. The observed deviation from this line for $T \geq 80°K$ can be attributed to volume changes. Certainly, no marked anharmonicity is observed within the temperature range investigated $(60°K \leq T \leq 373°K)$.

We conclude, therefore, that the results of Yaqub and Hohenemser, the thermal data, and the absence of strong anharmonic effects in the Debye-Waller factor for substances other than tin provide some indication

[15] D. L. Martin, Can J. Phys. **38**, 17 (1960).
[16] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).
[17] B. W. Batterman and D. R. Chipman, Phys. Rev. **127**, 690 (1962).

that the deviation from quasiharmonic theory observed by Boyle *et al.* cannot be attributed to anharmonic effects.

APPENDIX

At $T=0$ the Grüneisen parameter $\gamma(T)$ is given by

$$\gamma_0 = -\lim_{T \to 0}[(\partial \ln\Theta^c/\partial \ln V)_T], \qquad (A1)$$

$$= -\lim_{T \to 0}\left[\frac{1}{\beta}(\partial \ln\Theta^c/\partial T)_p\right].$$

In terms of the elastic constants, Θ^c at low T is expressed as

$$\Theta^c = \Theta^{el} = (h/k)(9N/4\pi V)^{1/3}\rho^{-1/2}a_0^{-1/3}. \qquad (A2)$$

Using, for example, the four-term approximation of Betts, Bhatia, and Horton,[18] we have

$$a_0 = (2f_A + f_B + 8f_C + 4f_E)/15,$$

---

[18] D. D. Betts, A. B. Bhatia, and G. K. Horton, Phys. Rev. **104**, 43 (1956).

where the f's are related to

$$\sum_{i=1}^{3} \frac{1}{v_i{}^3(\theta,\phi)}$$

in directions A, B, C, and E, defined by Betts *et al.*, and can be expressed in terms of the elastic constants, c_{ij}.

From (A2) one obtains

$$(\partial \ln\Theta^c/\partial T)_p = \beta/6 - (\tfrac{1}{3})(\partial \ln a_0/\partial T)_p,$$

and since $\gamma = \beta v/\kappa_s C_p$, Eq. (A1) can be written as

$$\gamma_0{}^2 + \gamma_0/6 = [V_0/3(\kappa_s)_0]$$
$$\times \{\lim_{T \to 0}[(\partial \ln a_0/\partial T)_p(1/C_v)]\}. \qquad (A3)$$

$(\kappa_s)_0$ is the value of the adiabatic compressibility at $T=0$. Hence, a knowledge of $a_0(T)$, or what is equivalent, $c_{ij}(T)$ at low temperatures will suffice to give γ_0.

Note added in proof. We have carried out similar calculations to obtain $\Theta^{DW}(T)$ for platinum, and found $\Theta_h{}^{DW} = 233 \pm 3°K$. In a recent Mössbauer experiment N. Koller and G. M. Rothberg[19] obtained $\Theta^{DW} = 240 \pm 8°K$ (assuming a total internal conversion coefficient $\alpha = 9$) in good agreement with the thermodynamic data.

---

[19] N. Koller and G. M. Rothberg, private communication and report to the Third International Mössbauer Conference, September 4-8, 1963, Ithaca, New York (unpublished).