

Critical Analysis of the Thermodynamic Data for Pt and a Prediction of $\Theta_{\text{DW}}(T)$

J. L. FELDMAN AND G. K. HORTON

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

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The available thermodynamic data for Pt are reviewed. A $\Theta^{\circ}(T)$ curve is constructed, and anharmonicity and volume expansion are explicitly allowed for. Values of $\langle\omega^n\rangle_{\text{av}}$ for both positive and negative n are derived and correlated in the usual way, by constructing a Barron plot. The $\Theta_{\text{DW}}(T)$ versus T curve is constructed by using a Padé approximant to link the high- and the low-temperature expansion. The resultant $\Theta_{\text{DW}}(T)$ is corrected for the volume expansion. Other anharmonic effects in $\Theta_{\text{DW}}(T)$ are neglected for $T \lesssim \Theta$. We find $\Theta_{\text{DW}}(0) = (232 \pm 3)^{\circ}\text{K}$ and $\Theta_{\text{DW}}(\infty) = (231 \pm 3)^{\circ}\text{K}$. These results are compared with experiment in the preceding paper by Harris, Benczer-Koller, and Rothberg.

I. INTRODUCTION

THE Mössbauer effect has recently been observed in platinum metal by Harris *et al.*¹ The fraction of recoilless γ rays is given by $f = e^{-2W}$, where $2W$ is the Debye-Waller factor. There are also a fair number of thermodynamic data available for Pt, and it has been shown how a suitable analysis² of such data yields³ $\Theta_{\text{DW}}(T)$, the Debye characteristic temperature of the Debye-Waller factor.

The purpose of this paper is a critical examination of the available measurements of the specific heat, thermal expansion, and compressibility of Pt to see whether we can make reliable predictions for the Debye-Waller factor. We find that although these data are by no means complete or consistent, it is nevertheless possible to predict $\Theta_{\text{DW}}(T)$. This results from the fact that $\Theta_{\text{DW}}(T)$ usually varies little with temperature and is not sensitive to the detailed properties of the vibrational density of states.

We use the quasiharmonic approximation by allowing for the effect of the thermal expansion of the crystal. A detailed comparison of our predicted values of Θ_{DW} is presented in the preceding paper.¹ Furthermore, if our estimate of Θ_{DW} is correct, it is then possible to extract from the Mössbauer measurements the relevant internal conversion coefficient more accurately than from the direct experiments.⁴

II. THERMODYNAMIC DATA

The specific heat of Pt has been tabulated by Simon and Zeidler⁵ in the range $10^{\circ}\text{K} \leq T \leq 1400^{\circ}\text{K}$. It has been measured by Kok and Keesom⁶ in the range

¹ J. R. Harris, N. Benczer-Koller, and G. M. Rothberg, *Phys. Rev.* **137**, A1101 (1965) (previous paper).

² J. L. Feldman and G. K. Horton, *Phys. Rev.* **132**, 644 (1963); T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 49; See also L. S. Salter (to be published); For a different approach see L. P. Potapov, *Fiz. Tverd. Tela* **5**, 1927 (1963) [English transl.: *Soviet Phys.—Solid State* **5**, 1408 (1964)].

³ The generally accepted notation is $\Theta^M(T)$. We use $\Theta_{\text{DW}}(T)$ to conform with the notation of the previous paper.

⁴ J. R. Harris, N. Benczer-Koller, and G. M. Rothberg (to be published).

⁵ F. Simon and W. Zeidler, *Z. Physik. Chem. (Leipzig)* **123**, 383 (1926). Their measurements are in the range $17.5^{\circ}\text{K} \leq T \leq 208.3^{\circ}\text{K}$.

⁶ J. A. Kok and W. H. Keesom, *Physica* **3**, 1035 (1936).

$1.2^{\circ}\text{K} \leq T \leq 20.3^{\circ}\text{K}$, by Clusius⁷ *et al.* in the range $10^{\circ}\text{K} \leq T \leq 273^{\circ}\text{K}$, by Ramanathan and Srinivasan⁸ in the range $1.3^{\circ}\text{K} \leq T \leq 4.2^{\circ}\text{K}$, and by Budworth *et al.*⁹ in the range $1.8^{\circ}\text{K} \leq T \leq 4.2^{\circ}\text{K}$. Hoare¹⁰ and his collaborators have also extended their measurements down to 1.3°K and have included both a T^3 and a T^5 term in addition to the usual $\gamma_{\text{el}}T$ term in the analysis of C_p . It is this most recent analysis that is quoted in the present paper.

The thermal expansion of Pt has been measured by Andres¹¹ and by Nix and McNair.¹² For the compressibility we used the value quoted by Clusius *et al.* The value quoted by Andres is 6% higher. The temperature dependence of the compressibility is not known, the quoted values being room-temperature values. Since the compressibility only enters in small correction terms, this uncertainty is not serious. For the $C_p - C_v$ correction we used Grüneisen's rule with a $\gamma = 2.8$. Even at room temperature, this correction is less than 2% of C_p .

In Fig. 1, we show $\Theta^{\circ}(T)$, the calorimetric equivalent Debye temperature. It is clear that the data do not all agree. We point out that the data have been obtained in different laboratories (in one case almost thirty years ago), with samples of rather different purity and preparation. We have assumed that the value for γ_{el} , the coefficient in the electronic term in the specific heat, lies between $(15.57 \pm 0.03)10^{-4}$ and $(15.96 \pm 0.10)10^{-4}$ Cal/ $^{\circ}\text{K}^2$ mole, the values found respectively by Hoare and by Ramanathan and Srinivasan. The value suggested by Kok and Keesom is 15.1 10^{-4} Cal/ $^{\circ}\text{K}^2$ mole. Rayne's¹³ value of $\gamma_{\text{el}} = (16.5 \pm 0.8)10^{-4}$ Cal/ $^{\circ}\text{K}^2$ mole is not incompatible with the above-mentioned values. The two solid curves in Fig. 1 for $T \lesssim 15^{\circ}\text{K}$ correspond to these two

⁷ K. Clusius, C. G. Losa, and P. Franzosini, *Z. Naturforsch.* **12**, 34 (1957).

⁸ K. G. Ramanathan and T. M. Srinivasan, *Proc. Indian Acad. Sci.* **A49**, 55 (1959).

⁹ D. W. Budworth, F. E. Hoare, and J. Preston, *Proc. Roy. Soc. (London)* **A257**, 250-6 (1960).

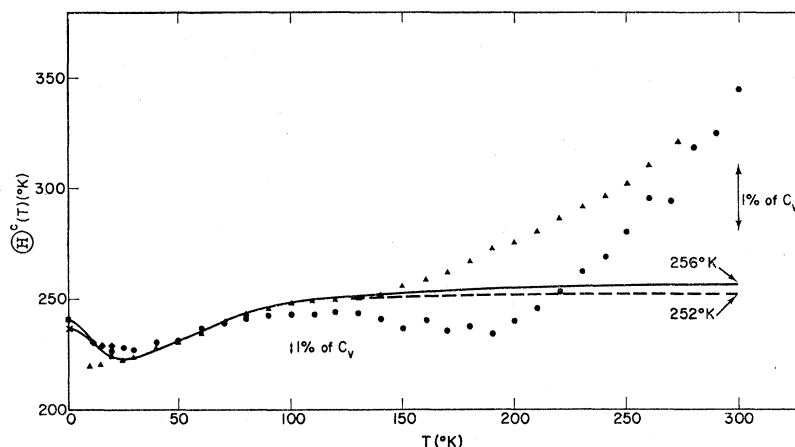
¹⁰ F. E. Hoare (private communication).

¹¹ K. Andres, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1962), p. 397.

¹² F. C. Nix and D. McNair, *Phys. Rev.* **61**, 74 (1942).

¹³ J. Rayne, *Phys. Rev.* **95**, 1428 (1954).

FIG. 1. Plot of $\Theta^e(T)$ versus T for Pt. The triangles are from Clusius *et al.*, the circles from Simon and Zeidler (tabulation), the diamonds from Kok and Keesom (data for $10^\circ\text{K} \leq T \leq 20^\circ\text{K}$), the square from Ramanathan and Srinivasan, and the cross from Budworth *et al.* Solid lines denote estimates of $\Theta^e(T)$ from all the experimental data (after removing the linear, i.e., anharmonic, term in T and correcting to 0°K volume). The two curves for $T \lesssim 15^\circ\text{K}$ are our estimates of the experimental limits in this temperature range. The dashed line is the same as the solid curve except for the volume correction.



γ_{e1} values and the associated Θ_0^e , respectively ($236.5 \pm 1.6^\circ\text{K}$) and ($239.6 \pm 2.4^\circ\text{K}$). We used $\gamma_{e1} = 15.96 \times 10^{-4} \text{ Cal}/^\circ\text{K}^2 \text{ mole}$ to correct the data of Clusius *et al.* for the electronic contribution.

Comments on the $\Theta^e(T)$ Data

(a) Kok and Keesom's data from 10 to 20°K are represented in Fig. 1 by the three diamonds. At lower temperatures their results are too scattered to be significant.

(b) Simon and Zeidler's tabulation is represented by the circles. We have rejected these data above 80°K in favor of the much more recent data of Clusius *et al.*

(c) There are two recent measurements of C_p near $T = 0^\circ\text{K}$.

The measurement of Hoare¹⁴ from $T = 1.3$ to 4.2°K was fitted to (in $\text{mJ}/\text{mole}^\circ\text{K}$) $C_v = \gamma_{e1}T + (124.83T/\Theta_0^e)^3 + \delta T^5$. We have already given their γ_{e1} and Θ_0^e ; their $\delta = 0.000170 \pm 0.00020 \text{ mJ}/^\circ\text{K}^{+5} \text{ mole}^{+1}$. The other measurement due to Ramanathan and Srinivasan was analyzed without a T^5 term and we estimate that if such a term had been included (and it should have been) they would have found 241.1°K for their Θ_0^e .¹⁵ We estimated $\Theta_{\text{DW}}(T)$ using both values of Θ_0^e , i.e., both the solid curves in Fig. 1. The difference between them is almost within the stated errors and leads to $\Theta_{\text{DW}}(T)$ curves that are indistinguishable.

(d) The data of Clusius *et al.* are represented by the triangles. On D. L. Martin's suggestion we have used these data down to 20°K . Below 20°K their results seem incompatible with the probable value of Θ_0^e . Similar difficulties with Clusius' calorimetric data below 20°K have been noted by Martin.¹⁶

¹⁴ We are indebted to Dr. Hoare for communicating his results to us before publication.

¹⁵ An analysis with and without a T^5 term was performed by Hoare on his data, and an increase in Θ_0^e of 1.6°K was the effect of including the T^5 term.

¹⁶ D. L. Martin, Proc. Phys. Soc. (London) 83, 99 (1964).

Analysis of the Composite $\Theta^e(T)$ Curve

We want to use the values of $\Theta^e(T)$ to predict those of $\Theta_{\text{DW}}(T)$. We have described the procedure in a previous paper.² The first step is to construct a Θ_n versus n curve.¹⁷ This curve will subsequently be referred to as a Barron plot. We define

$$k\Theta_n = \hbar \left\{ \frac{1}{3}(n+3) \langle \omega^n \rangle_{\text{av}} \right\}^{1/n}.$$

The average is taken over the vibrational spectrum. By plotting $[\Theta^e(T)]^2$ versus T^{-2} , after correcting $\Theta^e(T)$ to constant 0°K volume V_0 , one can obtain $\Theta_2 (= \Theta_\infty^e)$, Θ_4 , and make an estimate of Θ_6 . This is done in Fig. 2; the intercept of the straight line¹⁸

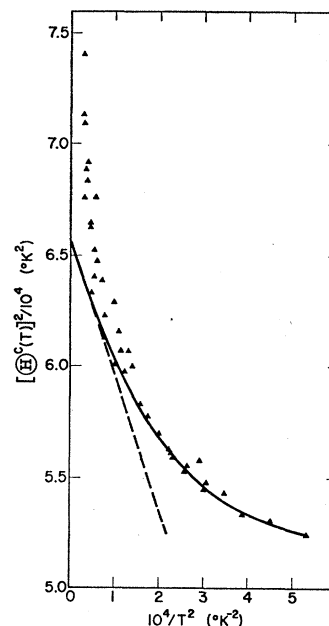


FIG. 2. Plot of $[\Theta^e(T)]^2$ versus $1/T^2$ for Pt. Points are from Clusius *et al.* (Θ^e corrected to the 0°K volume.)

¹⁷ T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) 242, 478 (1957).

¹⁸ The steep rise of the calorimetric data above the straight line for $T \rightarrow \infty$ is due to the well-known anharmonic term in C_v , linear in T . It is this term that we eliminate here.

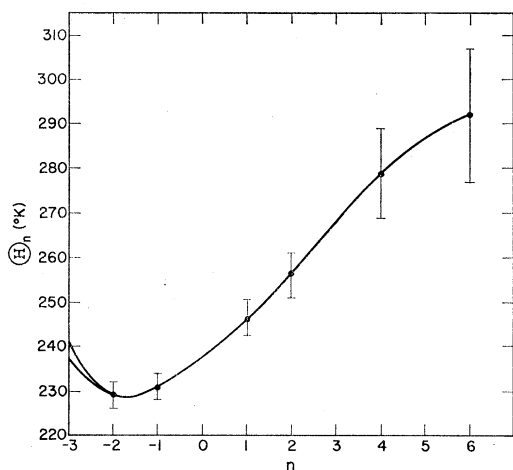


FIG. 3. Barron plot for Pt. Plot of Θ_n versus n , where $k\Theta^n = \hbar \left\{ \frac{1}{3}(n+3)(\omega^n)_{av} \right\}^{1/n}$; the moments refer to the 0°K volume. The two solid curves correspond to the uncertainty in Θ_0° (see text). The wings represent our estimate of the maximum effect of the uncertainty in the thermodynamic data. In the positive moments the wings represent our estimate of the maximum error caused by Clusius *et al.*'s experimental scatter. However, there may be additional uncertainty in the positive moments caused by anharmonicity.²⁰ $\Theta_{-1} = \Theta_{DW}(0)$ and $\Theta_{-2} = \Theta_{DW}(\infty)$.

yields Θ_2 , the slope Θ_4 and the deviation of the triangles from the straight line gives an estimate of Θ_6 .

We now have all the information required to draw $\Theta^\circ(T)_{\text{quasiharmonic}}$ with and without the above-mentioned correction to constant volume. The results are displayed in Fig. 1 by the solid and broken lines, respectively.

Additional Θ_n were obtained by methods described in Ref. 17. The results are displayed as typical Barron plots in Fig. 3. The two curves correspond to the two solid curves in Fig. 1. The wings on the experimental points correspond to our estimate of the uncertainty in the experimental data.

III. THE DEBYE-WALLER FACTOR

The temperature dependence of the Debye-Waller factor $2W$ should be displayed by plotting the appropriate equivalent Debye temperature $\Theta_{DW}(T)$. We do this in Fig. 4. The broken line displays the effect of the volume expansion. In our earlier paper² we gave only the low- and high-temperature expansions for $\Theta_{DW}(T)$.

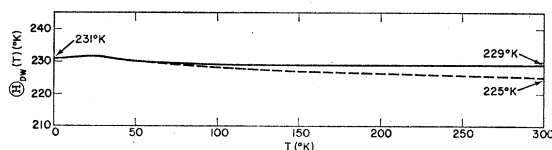


FIG. 4. Plot of $\Theta_{DW}(T)$ versus T . The solid line gives the value of $\Theta_{DW}(T)$ referred to the 0°K volume. The broken line gives the effect of thermal expansion.

In this work we used a (4,4) Padé approximant to find $\Theta_{DW}(T)$ at intermediate temperatures. We estimate the error due to the use of the Padé approximant to be less than 1%.¹⁹

Although we have not explicitly included vibrational anharmonic terms in the calculation these have nevertheless been included in an approximate way. Barron²⁰ has shown that vibrational anharmonicity in the entropy of a crystal lattice can be described by an *effective* frequency spectrum. At low T , this spectrum is temperature-independent and hence the specific heat at low T can also be described by it. The negative moments which are determined mainly by the low-temperature calorimetric data can therefore be assumed to refer to the $T=0^\circ\text{K}$ effective spectrum. If in addition we assume that vibrational anharmonicity in the Debye-Waller factor can be described by the same effective spectrum as for the entropy²¹ then it follows that $\Theta_{DW}(T)$ at low T is correctly given by Θ_{-1} found from the thermal data. At general temperatures Barron has shown how to get a rough estimate of vibrational anharmonic effects in Θ° and hence Θ_{DW} from C_p data. For platinum, the size of this effect is less than the volume effect but tends to oppose it, yielding a $\Theta_{DW}(T, V_T)$ curve which is flatter than the one we have drawn.

From Fig. 3 we estimate the uncertainty in $\Theta_{DW}(0)$ and $\Theta_{DW}(\infty)$ is $\pm 3^\circ\text{K}$. The temperature variation in $\Theta_{DW}(T)$ at V_0 (about 1%) is an order of magnitude smaller than that of $\Theta^\circ(T)_{q-h}$ at V_0 . It is about half that observed for other metals.⁴

To improve substantially on the uncertainty in $\Theta_{DW}(T)$ requires new precise measurements of the specific heat, the compressibility, and the lattice parameter from 0°K to room temperature. Values of the elastic constants at low T would serve to fix θ° ; these elastic constants have not yet been measured.

ACKNOWLEDGMENTS

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This work was supported by a grant from the U. S. Air Force Office of Scientific Research.

¹⁹ C. Domb and C. Isenberg, Proc. Phys. Soc. (London) **79**, 659 (1962); L. S. Salter (to be published). Note that the coefficient of $[\Theta_{DW}(\infty)/T]^8$ in the high-temperature expansion of $[\Theta_{DW}(T)/\Theta_{DW}(\infty)]^2$ is

$$A_2^2 - \frac{1}{3600}A_2 + \frac{1}{10,886,400} \left[\left(\frac{\Theta_2}{\Theta_{-2}} \right)^6 - 1 \right],$$

and

$$A_2 = \frac{1}{3600} \left[\left(\frac{\Theta_2}{\Theta_{-2}} \right)^2 - 1 \right].$$

²⁰ T. H. K. Barron (to be published).

²¹ T. H. K. Barron (private communication).