Temperature Dependence of the Debye-Waller Factor of Platinum†

J. R. HARRIS, N. BENCZER-KOLLER, AND G. M. ROTHBERG
Department of Physics, Rutgers University, New Brunswick, New Jersey
(Received 2 September 1964)

The Mössbauer absorption spectrum of the 99-keV gamma ray of Pt^{195} in platinum metal has been studied from 20 to 100°K. In a separate experiment to be published later, the internal-conversion coefficient α was found to be $\alpha=7.2\pm0.7$. Using this value of α the fraction of recoilless emission f_e and recoilless absorption f_a are $f_e(20°K)=0.089\pm0.002$, $f_e(77°K)=0.021\pm0.003$, and $f_a(20°K)=0.129\pm0.008$, $f_a(77°K)=0.043\pm0.011$. The half-life of the 99-keV level is $\tau_{1/2}=(1.7\pm0.2)10^{-10}$ sec in agreement with the electronic measurement $\tau_{1/2}\approx1.4\times10^{-10}$ sec. The Debye temperature θ_{DW} determined from the Debye-Waller factor is in good agreement with a calculation based on the quasi-harmonic approximation. The Debye temperature extrapolates to $\theta_{DW}=(234\pm6)°K$ at 0°K and is essentially independent of temperature up to 100°K.

I. INTRODUCTION

PLATINUM^{195} is an interesting candidate for Mössbauer-effect studies from the point of view of both nuclear structure and solid-state investigations. According to the presently accepted decay scheme of the parent Au^{195} there are two ground-state transitions of 99 and 130 keV, respectively, both of which may in principle be used for recoilless resonance experiments. The interest in the solid-state properties of platinum metal lies mainly in the fact that magnetic properties of platinum alloys have been relatively neglected compared with the iron group metals and alloys, and in the study of platinum metal lattice dynamics. In this paper the absorption spectrum of the 99-keV gamma ray was investigated using platinum metal sources and absorbers.[1] The Debye-Waller factor was determined from 20 to 100°K and was compared with a semiempirical prediction based upon heat capacity measurements.[2] The Debye-Waller factors determined by Mössbauer techniques depend, however, in a very sensitive way on the exact value of the internal conversion coefficient α of the transition under consideration. Previous determinations of α varied from $\alpha=7.1$ to 10.2.[3] In view of the large latitude present in α, the Au^{195} decay scheme and in particular the internal conversion coefficient of the 99-keV transition were redetermined in a separate experiment which will be described in a subsequent paper.[4]

The fraction f of recoilless gamma rays emitted or absorbed by a nucleus in a crystal lattice is e^{-2W}, where $2W$ is the Debye-Waller factor, which for a cubic lattice with one atom per unit cell is given by

$$2W=\frac{2R}{\hbar^2}\int_0^{\omega_m}\omega^{-2}G(\omega)\left[\tfrac{1}{2}\hbar\omega+\hbar\omega/(e^{\hbar\omega/kT}-1)\right]d\omega. \quad (1)$$

Here R is the recoil energy $E_0^2/2mc^2$, E_0 is the gamma-ray energy, ω_m is the maximum frequency of the lattice, and $G(\omega)$ is the frequency distribution normalized so that $\int_0^{\omega_m}G(\omega)d\omega=1$. If the lattice is assumed to have a Debye frequency spectrum with $\omega_m=k\theta_{DW}/\hbar$, then

$$2W=\frac{6R}{k\theta_{DW}}\left[\frac{1}{4}+\left(\frac{T}{\theta_{DW}}\right)^2\int_0^{\theta_{DW}/T}\left[\frac{x}{(e^x-1)}\right]dx\right], \quad (2)$$

where θ_{DW} is the effective Debye temperature appropriate to $2W$. Since the real frequency spectrum may be considerably different from a Debye spectrum, the effective Debye temperature appropriate to any other quantity involving a different average over the spectrum may be appreciably different from θ_{DW}. Thus for example the Debye temperature θ_c pertinent to the heat capacity will generally vary much more rapidly with temperature than θ_{DW}. In principle, however, from knowledge of the heat capacity, lattice constant and elastic constants as functions of temperature, one can learn enough about the frequency spectrum to predict the quasiharmonic Debye-Waller factor. Provided the input data are accurate enough and the theoretical interpretation is correct, this prediction can be made with an accuracy better than most measurements of $2W$.

For the Mössbauer effect reliable predictions of $2W$ would be very useful. From the absorption spectrum one can determine $f/(1+\alpha)$, where α is the internal conversion coefficient, and a knowledge of f would make it possible to determine α with an accuracy about as good as the best direct determinations. Also since θ_c and θ_{DW} can be very different, a knowledge of θ_{DW} would help in choosing a suitable host lattice in which to embed radioactive nuclei. On the other hand, if α is known well enough, it is not too difficult to determine f with sufficient accuracy to check the theory. So far predictions of Debye-Waller factors from heat-capacity data have been made only for copper, germanium,

† This research was supported by the National Science Foundation.

[1] A preliminary report of this work was given at the Third International Mössbauer Conference. See G. M. Rothberg, Benczer-Koller, and J. R. Harris, Rev. Mod. Phys. **36**, 357 (1964). Similar results were also reported by A. B. Buyrn, Bull. Am. Phys. Soc. **9**, 411 (1964).

[2] J. L. Feldman and G. K. Horton, Phys. Rev. **132**, 644 (1963), also following paper, *ibid.* **137**, A1106 (1965).

[3] *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences—National Research Council, Washington 25, D. C.), NRC 61-4-100.

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

silicon,[5] and β tin (metal).[2] These calculations make use of the harmonic or quasiharmonic approximations. In the former the lattice potential is assumed to be harmonic, while in the latter it is assumed that of all the anharmonic effects only the thermal expansion needs to be taken into account. In the case of copper and with use of the quasiharmonic approximation, agreement between calculated and x-ray values of θ_{DW} is well within the experimental uncertainty of about ± 15°K. In germanium and silicon with use of the harmonic approximation and assuming constant volume equal to the volume at 0°K, the predicted[5] high-temperature values of θ_{DW} are (297 ± 3) and (531 ± 5)°K, respectively. The correction for volume expansion will somewhat reduce these values. The x-ray measurements of the Debye-Waller factor cover the range 300 to 1100°K and yield constant values of θ_{DW} for germanium and silicon of (290 ± 5) and (543 ± 8)°K, respectively.[6] These predicted and experimental values are in apparent agreement. However, anharmonic effects are very prominent in the high temperature C_V data for germanium. It is not known how anharmonic contributions to θ_{DW} at high temperatures can be calculated from the C_V data. Until it can be shown that anharmonic effects in θ_{DW} for germanium are quite small (a few percent), even at high temperatures ($T \gg \theta$), the good agreement between theory and experiment mentioned above may be entirely fortuitous.

Measurements over an extensive temperature range have been made in the case of polycrystalline tin.[7] However, metallic tin is exceptional in several respects. The crystal lattice is not cubic but tetragonal, and so for single crystals the Debye-Waller factor depends upon the direction of the wave vector of the radiation with respect to the crystal axes and is not given by Eq. (1). Calculations of θ_{DW} are normally made for single crystals, and an average has to be taken to compare the calculated values with the experiments in polycrystals. In the calculation[2] of θ_{DW} this averaging was done in an approximate way. Furthermore, since the lattice is tetragonal there exists the possibility of a small, but non-negligible, unresolved quadrupole splitting of the Mössbauer spectrum which could affect the interpretation of the data. It is therefore desirable to determine the Debye-Waller factor of platinum metal as a function of temperature; the lattice is cubic, and θ_{DW} has been calculated from heat capacity data in the range $0 \lesssim T \lesssim \theta_c$.

[5] T. H. K. Barron, M. L. Klein, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, *Proceedings of the Eighth Internationa Conference on Low Temperature Physics* (Butterworths Scientific Publications, Ltd., London, 1963), p. 415; 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; P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. 4, 273 (1959).

[6] B. W. Batterman and D. R. Chipman, Phys. Rev. **127**, 690 (1962).

[7] A. J. F. Boyle, D. St. P. Banbury, C. Edwards and E. H. Hall, Proc. Phys. Soc. (London) **77**, 129 (1961) C. Hohenemser, Ph.D. dissertation, Washington University, 1963 (unpublished).

II. APPARATUS

The source was prepared by electroplating 3 mCi of carrier-free Au^{195} on a 0.001-in.-thick natural platinum foil (33.6% Pt^{195}), and annealing for over 12 h at 1000°C in a hydrogen atmosphere. It was reannealed at a later time with no change in the results. The absorbers were all stacked natural platinum foils, each either 0.001 in. or 0.005 in. thick, assembled in various combinations depending on the total thickness desired for a particular run. The interchangeability of these foils was checked.

The measurements were carried out in a cryostat equipped with thin windows at the bottom, a 0.040-in. beryllium foil sealing the low-temperature can and a 0.003-in. aluminized Mylar foil sealing the nitrogen-cooled vacuum jacket. The details of the cryostat are shown in Fig. 1. The motion of the source was provided by a dual coil 8CH8 University loudspeaker located at the top of the cryostat. The transfer tube with which nitrogen or hydrogen were transferred to the low temperature can could fit through the middle of the loudspeaker. The source was attached to a glass rod, approximately as long as the low-temperature can, which connected to a stainless steel tube rigidly attached to the loudspeaker. The source therefore moved through the cooling liquid. The absorber was rigidly clamped between two brass rings in the vacuum space below the beryllium window. These rings were connected to the low-temperature can by three rods which could be

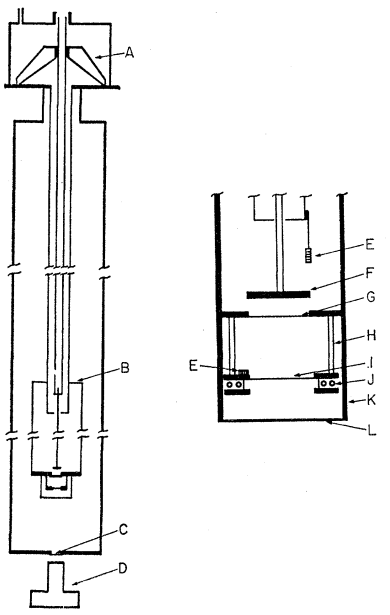

FIG. 1. Details of the cryostat and loudspeaker driving mechanism. (A) Dual voice coil loudspeaker; (B) low-temperature can; (C) aluminized Mylar window; (D) scintillation detector; (E) carbon thermometer; (F) source holder; (G) beryllium window; (H) copper or stainless steel rods; (I) absorber; (J) absorber heater; (K) copper radiation shield; (L) aluminum foil.

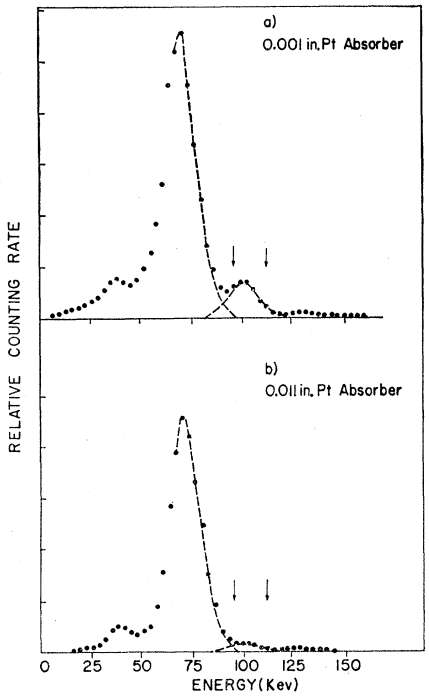

FIG. 2. γ-ray scintillation spectrum taken (a) with a 0.001-in. thick platinum absorber; (b) with a 0.011-in.-thick absorber.

either copper, solid stainless steel, or hollow stainless steel depending on the absorber temperature required. A heater consisting of a 1-in. diameter coil of wire was in contact with the absorber. Carbon thermometers were located immediately above the source and on the absorber holder. The source temperature was therefore always at the bath temperature, namely 77 or 20°K, however the absorber temperature was varied from 20 to 120°K. A cylindrical copper radiation shield, attached to the low-temperature can and with an aluminium foil window, surrounded the absorber holder.

The loudspeaker was driven at 7 cps by a parabolic signal applied to one of the coils, the parabolic wave form being produced by integration of the triangular output of a signal generator. The velocity of the speaker pickup coil generated a signal of triangular wave form which was fed back to the input of the integrator circuit.[8] The triangular pickup signal was also amplified in a Philbrick operational amplifier and displayed on a multichannel analyzer with a split memory. In one-half of the memory were fed the random pulses from a radioactive source while the Pt^{195} radiation triggered the second half of the memory. All data were normalized by dividing the counts accumulated in the second half by those accumulated in the first, thus correcting for vibrations and rubbing which somewhat distorted the parabolic waves.

The loudspeaker sensitivity was calibrated by observing the spectra obtained with a Co^{57} source embedded in a stainless steel matrix and iron and Fe_2O_3 absorbers for various gains of the Philbrick amplifier.

The detector consisted of a 1.5-in. diameter by 2-in. thick NaI (Tl) crystal mounted on an RCA 6342 photomultiplier.

III. RESULTS AND ANALYSIS

The scintillation spectrum obtained with the source in the cryostat, the detector 17 cm below and a 0.001-in. thick platinum foil absorber is shown in Fig. 2(a). In Fig. 2(b) is shown the spectrum obtained with the thickest absorber that was used in this experiment, $t_a=0.011$ in. The dashed curve is a Gaussian fit to the strong K x-ray peak, and is shown to demonstrate that there is negligible x-ray background contribution under the 99-keV line within the window selected and indicated by the two vertical arrows. Unfortunately platinum acts as a critical absorber for the 99-keV gamma ray, and therefore the maximum absorber thickness that is convenient to use and still have a clear resolvable spectrum and a reasonable counting rate at 99 keV is just about 0.011 in.

The velocity spectra of recoilless emission and absorption of the 99-keV transition were measured both as a function of absorber thickness with the source and absorber at the same temperature, 20 or 77°K, and as a function of absorber temperature with the source at 20°K and an absorber of fixed thickness. Typical spectra are shown in Fig. 3.

The size of the effect $\epsilon=[N(v=\infty)-N(v=0)]/N(v=\infty)$ and the width Γ of the absorption line at half-maximum were determined for each curve by matching by eye the experimental data with a set of Lorentzian curves of various thicknesses and depths. The errors on the quoted values for ϵ and Γ were obtained from the difference in ϵ between the Lorentzian curve that matched the data and the two extreme curves

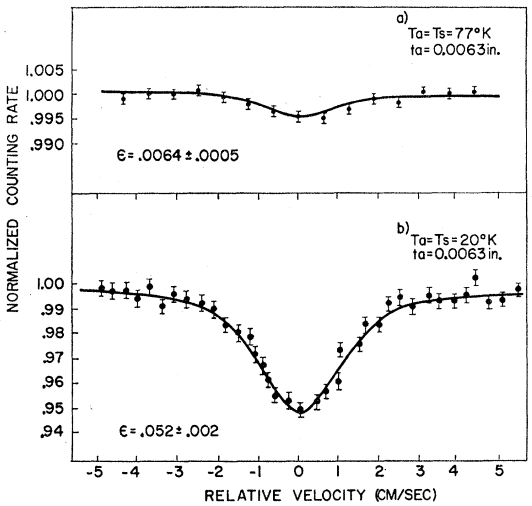

FIG. 3. Typical Mössbauer spectra.

[8] G. Wertheim (private communication).

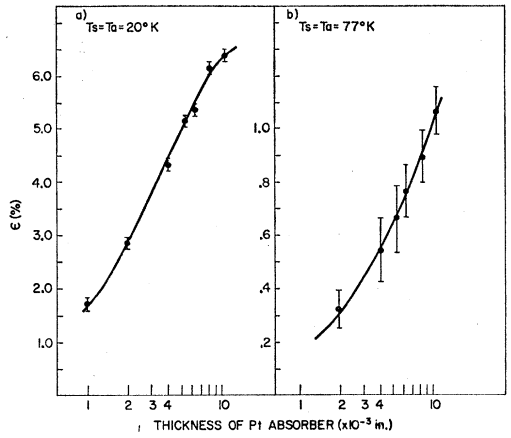

FIG. 4. Plot of the Mössbauer effect $\epsilon=[N(V=\infty)-N(V=0)]/N(V=\infty)$ versus the logarithm of the absorber thickness.

that just could not fit the experimental points. These determinations were checked and confirmed in several cases by fitting the experimental points to Lorentzian curves by the least-squares method.

The values of ϵ thus obtained for the first set of experiments where source and absorber were kept at the same temperature but the thickness of absorber was varied, were plotted versus the logarithm of the absorber thickness [Figs. 4(a) and 4(b)].

A family of theoretical curves $\epsilon=f_s[1-J_0(ix/2)e^{-x/2}]$ were also plotted versus the logarithm of the effective absorber thickness $x=na\sigma_0 t_a f_a/(1+\alpha)$ for various f_s, the fraction of recoilless emission by the source. In these expressions n is the number of atoms per cm^3 in the absorber, a the natural abundance of Pt^{195}, $\sigma_0=5\times10^{-19}$ cm^2 the cross section for Mössbauer absorption, t_a the absorber thickness in cm, and f_a the fraction of recoilless absorption for the absorber. The above formula for ϵ is only correct for a thin source and therefore is valid in the present case since $na\sigma_0 t_s f_s/2<0.04$.[9]

It was determined that the Au^{195} activity had diffused into the 0.001-in. platinum foil to a depth of about 0.002 in. by observing the transmission of x rays and 99-keV gamma rays through the front and the back surfaces.

The experimental curves were then compared with the theoretical ones by sliding over the horizontal scale. The best fit to the theoretical curves yielded values for quantities called f_{s0} and f_{a0}, the true values being $f_s=f_{s0}+\delta_s$ and $f_a=f_{a0}+\delta_a$. The theoretical expression for ϵ was expanded in a Taylor series about δ_s and δ_a keeping only the terms linear in δ_s and δ_a. This expression could then be analyzed by the least-squares method, yielding δ_s and δ_a as well as the errors in the determination of f_s and f_a.

[9] S. Margulies and J. R. Ehrman, Nucl. Instr. Methods **12**, 131 (1961).

The final results, assuming $\alpha=7.2$,[4] were

$$f_s(20°K)=0.089\pm0.002, \quad f_a(20°K)=0.129\pm0.008,$$
$$f_s(77°K)=0.021\pm0.003 \text{ and } f_a(77°K)=0.043\pm0.011.$$

The variation of the width Γ of the resonant line with absorber thickness is shown in Figs. 5(a) and 5(b). The experimental points were fitted by least squares to a straight line. The values obtained for the slopes of these lines agree well with those predicted by Margulies and Ehrman.[9] The extrapolation of these lines to zero absorber thickness gives a measurement of at least the lower limit of the half-life of the 99-keV state. The half-life $\tau_{1/2}=(1.7\pm0.2)10^{-10}$ sec determined in this manner is an average of the values obtained at 20 and at 77°K, $\tau_{1/2}(20°K)=(1.6\pm0.2)\times10^{-10}$ sec and $\tau_{1/2}(77°K)=(1.73\pm0.3)\times10^{-10}$ sec and agrees with the electronic measurement $\tau_{1/2}\approx1.4\times10^{-10}$ sec.[10]

In the second set of experiments, the source was kept at 20°K, and the temperature of the 0.005-in. thick absorber was varied from 20 to 100°K.

The experimental results of $\epsilon(T)/f_s$ obtained for various absorber temperatures were plotted on a graph of the theoretical expression $[1-J_0(ix/2)e^{-x/2}]$ versus x. Thus an $x=(na\sigma_0 t_a f_a)/(1+\alpha)$, and hence f_a and the Debye-Waller factor $2W$ were obtained for each temperature and an assumed conversion coefficient.

From a plot of $2WT$ versus T/θ, where

$$2WT=\frac{6RT}{k\theta_{DW}}\left[\frac{1}{4}+\left(\frac{T}{\theta_{DW}}\right)^2\int_0^{\theta_{DW}/T}\left[\frac{x}{(e^x-1)}\right]dx\right], \quad (3)$$

a unique value of θ_{DW} can be obtained for each temperature. A compilation of these results is shown in Fig. 6. The Debye temperature was calculated for each temperature for $\alpha=7.2$, as well as for $\alpha=6.0$ and $\alpha=8.0$ for comparison. From these plots it can be seen that the absolute value of θ as well as the temperature dependence are sensitive to the value of α chosen. The

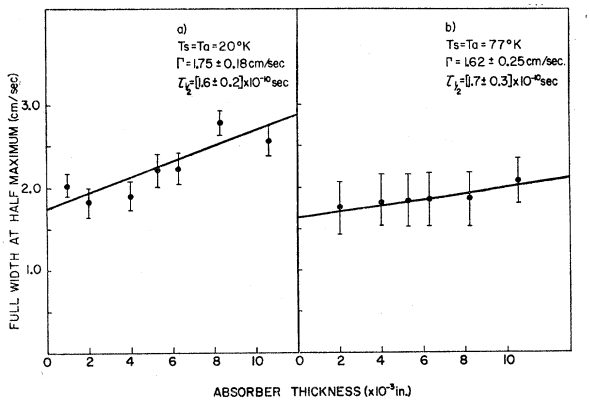

FIG. 5. Variation of the width of the resonant line with absorber thickness.

[10] A. E. Blaugrund, Phys. Rev. Letters **3**, 226 (1959).

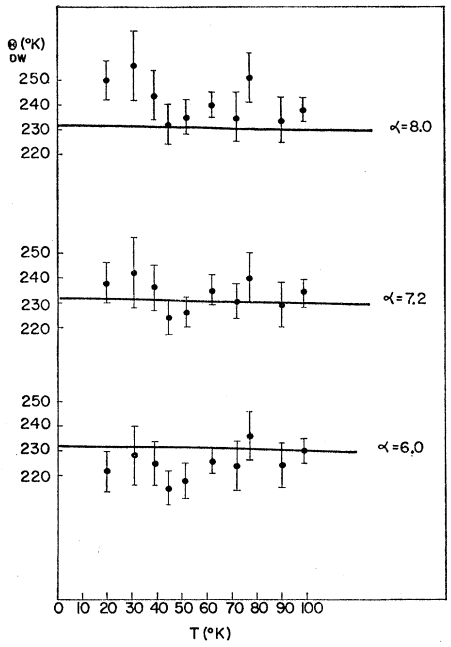

FIG. 6. Experimental values of θ_{DW} for various values of the internal conversion coefficient versus temperature. The solid line was obtained from the analysis of specific heat measurements and other thermodynamic data (Ref. 2).

solid line was obtained by Feldman and Horton[2] from an analysis of specific-heat measurements which will be discussed in the next section.

In order to check whether there was no appreciable line broadening with corresponding reduction in the resonance effort ϵ, the areas under the absorption curves for different temperatures were compared. For thin source and absorber the area under the absorption curve is proportional to $f_s f_a$ independent of line broadening. Since the data are excellent fits to Lorentzians, the area A was taken to be $A=(\frac{1}{2}\pi)\Gamma\epsilon$. For fixed-source temperature the ratio of any areas is the same as the ratio of the corresponding f_a. These area ratios indeed agreed well within the experimental accuracy with the ratios of the f_a obtained from the analysis described originally for temperatures from 45 to 100°K. Below 45°K the absorber can no longer be considered thin. Similarly for the same absorber thickness and temperature the ratio of areas is the same as the ratio of the corresponding f_s. This check was carried out for source temperatures of 20 and 77°K and absorber temperature of 77°K, and again the two ratios agreed to within 10%.

IV. CONCLUSIONS

Feldman and Horton[2] have calculated the temperature dependence of the effective Debye-Waller factor $2W$ and the Debye temperature θ_{DW} in the quasi-harmonic approximation for platinum. Their conclusions are that the Debye temperature should be $\theta_{DW}=(231\pm3)$°K at 0°K where the error stems from the experimental uncertainty in the specific-heat measurements, and should have a very slight temperature dependence as shown by the solid line on Fig. 6. From the present experiment the following conclusions can be drawn.

(1) Given a conversion coefficient $\alpha=7.2$, the Debye temperature extrapolates to $\theta_{DW}=(234\pm6)$°K at 0°K. At higher temperatures up to $T\approx\theta_{DW}/2$, θ_{DW} is also in good agreement with Feldman and Horton's predictions. The Mössbauer effect at much higher temperatures is extremely small in the case of Pt^{195} and reliable measurements could not be taken. Furthermore, it appears that it is possible to achieve a much higher precision in the determination of Debye-Waller temperatures by Mössbauer absorption techniques, namely $\pm3\%$ for the present case, than has been possible previously by x-ray scattering studies as in the case of copper, where θ_{DW} was only determined to within $\pm15\%$.

(2) Conversely, the experimental values of $f_a(T)/(1+\alpha)$ can be fitted to the theoretical predictions of $f=e^{-2W}$ by Feldman and Horton. This fit yields a more precise value of the conversion coefficient of the 99-keV transition in Pt^{195}, $\alpha=7.0\pm0.3$, than has been obtained so far by other direct methods. This new method for finding α is applicable because the measurements were made at low temperatures, where the theoretical predictions of $2W$ are known to be reliable, as shown in the following paper.[2]

ACKNOWLEDGMENTS

We wish to thank Professor G. K. Horton and J. Feldman for many helpful discussions, and R. Feldman for his aid in taking data.