Precision Determinations of the Mössbauer Recoilless Fraction for Metallic Gold in the Temperature Range $4.2 \leq T \leq 100\,^{\circ}\mathrm{K}$*

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Mössbauer spectra for thick gold absorbers have been measured as a function of absorber temperature T in the range $4.2 \leq T \leq 100\,^{\circ}\mathrm{K}$. By fitting these spectra with an appropriate theoretical line-shape function, values of $f(T)/(1+\alpha)$ have been obtained, where $f(T)$ is the recoilless fraction for metallic gold and α is the internal-conversion coefficient for the 77.3-keV state in Au^{197}. The precision in these values is about 1%, except at the higher absorber temperatures. Because of its importance in the thick-absorber line-shape analysis, the natural linewidth Γ_0 for the 77.3-keV state has been redetermined to be 0.923 ± 0.006 mm/sec. Values of $f(T)$ for metallic gold have been obtained by reducing our thick-absorber data with $\alpha = 4.30$. This value of α is based on two independent estimates which show good agreement. One estimate uses conversion-intensity data and theoretical internal-conversion coefficients, while the other estimate uses our $f(T)/(1+\alpha)$ data and predictions of $f(T)$ from a recent quasiharmonic analysis of gold thermodynamic data. The recoilless fraction for metallic gold as determined in our treatment is found to vary from $f(4.2\,^{\circ}\mathrm{K}) = 0.189$ to $f(100\,^{\circ}\mathrm{K}) = 0.0097$. Effective Debye temperatures $\Theta^M(T)$ are determined from these recoilless fractions for gold and are compared with corresponding effective Debye temperatures $\Theta^C(T)$ determined from specific-heat measurements.

I. INTRODUCTION

The temperature-dependent Mössbauer recoilless fraction $f(T)$ is the probability for recoilless absorption or emission of a resonance γ ray by a nucleus bound in a lattice. Since $f(T)$ values give information specific to a Mössbauer atom coupled to a host lattice, measurements of f are of particular value in the study of metallic binding in alloys, especially in alloys where the Mössbauer atom is an impurity. We are interested in studying the binding of gold in alloys using recoilless fraction determinations for Au^{197}, one of the heavier Mössbauer nuclides. To provide a basis for these gold-alloy studies, we have determined values of $f(T)/(1+\alpha)$ for pure gold in the temperature range $4.2 \leq T \leq 100\,^{\circ}\mathrm{K}$, where α is the internal-conversion coefficient for the 77.3-keV γ-ray transition in Au^{197}. Values of $f(T)$ for pure gold and information about α have been obtained from these $f(T)/(1+\alpha)$ measurements. It is these pure-gold results which are reported here.[1]

To adequately study metallic binding using f data, a high precision of measurement is needed. Such high precision has been attained in $f(T)$ measurements for Fe^{57} as a dilute source impurity in a variety of metallic hosts[2-4] through the use of the "black" absorber technique.[5,6] We have attained a precision of about 1% for values of $f(T)/(1+\alpha)$ for pure gold and certain gold alloys[7] by fitting an appropriate theoretical line-shape function to measured thick-absorber spectra. This precision is comparable to that attained in the Fe^{57} "black" absorber studies.

Determination of absolute recoilless fractions for gold from our treatment requires a knowledge of α. Two independent estimates for α are reported here. One estimate makes use of measured conversion-electron intensities and theoretical internal-conversion coefficients. The other estimate uses our $f(T)/(1+\alpha)$ data for pure gold and gold $f(T)$ values predicted from the results of a recent quasiharmonic analysis of thermodynamic data. These estimates will be seen to be in good agreement and are used to select a value of α which is used to deduce values of $f(T)$.

An effective Debye temperature $\Theta^M(T)$ can be used as a parameter to characterize a determination of $f(T)$; likewise $\Theta^C(T)$ can be used to characterize a determination of the lattice contribution to the specific heat at a temperature T. In the following, we contrast $\Theta^M(T)$ for metallic gold as determined from our deduced values of $f(T)$ with corresponding values of $\Theta^C(T)$ determined from specific-heat measurements. This comparison graphically illustrates the different ways in which the recoilless fraction and the lattice specific heat depend on the vibrational spectrum of a solid. Such a comparison for gold is of additional interest because of the unusual temperature dependence of $\Theta^C(T)$ below 15 °K as determined from measurements of Martin.[8,9]

II. LINE-SHAPE ANALYSIS

Values of $f(T)/(1+\alpha)$ for pure gold have been obtained from least-squares fitting a theoretical line-shape function to measured absorption line shapes for thick gold absorbers. The theoretical line shape used in the fitting procedure, which accounts for finite absorber thickness, is written as

$$N(v_s) = [N_\gamma(\infty) + N_x(\infty)]\left(1 - f'\frac{N_\gamma(\infty)}{N_\gamma(\infty)+N_x(\infty)} + f'\frac{N_\gamma(\infty)}{N_\gamma(\infty)+N_x(\infty)}\,\frac{2}{\pi\Gamma_0} \times \int_{-\infty}^{\infty} dv\,\frac{\exp\{-T_A/[4(v-v_0)^2/\Gamma_0^2+1]\}}{4(v-v_s)^2/\Gamma_0^2+1}\right). \tag{1}$$

This line-shape function describes a single, unsplit Mössbauer absorption spectral line obtained experimentally by moving a source relative to an absorber. In Eq. (1), $N(v_s)$ is the measured transmission, integrated over the running time of an experiment. It is a function of v_s, the relative Doppler velocity between the source and absorber. $N_\gamma(\infty)$ is the integrated transmitted intensity of 77.3-keV γ rays and $N_x(\infty)$ is the integrated transmission of other radiation which would be detected at $v_s=\infty$. The source recoilless fraction f' is the fraction of 77.3-keV γ rays which are emitted recoillessly. v is an integration variable and v_0 is the center of the absorption line relative to $v_s=0$. Γ_0 is the natural linewidth of the 77.3-keV γ-ray transition in velocity units.

The absorber effective-thickness parameter is represented in Eq. (1) by T_A. Since natural gold consists of only one stable isotope, Au^{197}, the gold-absorber effective thickness can be written as

$$T_A(T) = f(T)t_0\sigma_0/(1+\alpha)\ . \tag{2}$$

The areal density of gold in an absorber is given by t_0. The maximum resonance cross section[10] per unit mass of gold σ_0 is given by

$$\sigma_0 = \frac{\lambda^2}{2\pi m}\,\frac{2I^*+1}{2I+1}\ , \tag{3}$$

where λ is the wavelength of the 77.3-keV γ ray, $I^*=\frac{1}{2}$ is the nuclear spin of the first excited state in Au^{197}, $I=\frac{3}{2}$ is the spin of the ground state in Au^{197}, and m is the mass of a gold atom.

The transmission function in Eq. (1) is consistent with the general formulation of Margulies and Ehrman[11] under the following assumptions: (i) The radioactive emitters in the source are distributed uniformly, (ii) self-absorption in the source of the emitted recoilless γ rays occurs only through nonresonant electronic processes, and (iii) Γ_0 is independent of solid-state effects such that Γ_0 is the same in both the source and the absorber.

The shape of an absorption line, described by Eq. (1), is determined by the natural linewidth Γ_0 and the absorber effective-thickness parameter T_A. A value for $T_A(T)$, and therefore for $f(T)/(1+\alpha)$, is uniquely determined from a fit of Eq. (1) to a measured line shape for a given value of Γ_0. Because the above procedure used to determine $f(T)/(1+\alpha)$ is sensitive to the value used for Γ_0, a special determination of Γ_0 has been made in this study, which will be described in Sec. V.

III. EQUIPMENT AND EXPERIMENTAL PROCEDURES

The Mössbauer sine-wave transducer, associated electronics, and the data-handling techniques used in these measurements are similar to those which we have described previously.[12,13] A gold absorption spectrum and also a six-line Fe^{57} spectrum, used for the calibration of the velocity scale, were simultaneously measured using the same transducer. These spectra were collected using a multichannel analyzer operated in the pulse-height mode. The Fe calibration spectrum was obtained using a Co^{57} in Cu source and an annealed Armco iron absorber, both at room temperature.

A source of the 77.3-keV γ rays was at 4.2 °K for each of the measurements. The gold absorber used in a particular measurement was mounted in an evacuated cell immersed in liquid helium. The absorber, thus thermally isolated from the liquid-helium bath, was held at a specified temperature above 4.2 °K by controlling the current through a Nichrome wire heater on the absorber mounting. An absorber temperature was maintained to within 0.3% or less in the range 4.2–100 °K during a typical experimental running time of 12–15 h.

Determination of the absorber temperature was made by means of a CryoCal, Inc. germanium resistance thermometer in the range 4.2–50 °K and by means of a Rosemount Engineering Co. platinum resistance thermometer in the range 40–100 °K. Calibration, traceable to the National Bureau of

Standards, was supplied for each thermometer by the respective manufacturers.

IV. ABSORBERS AND SOURCES

The gold absorbers were circular disks whose thicknesses were obtained by either rolling or machining standard sheet stock of 99.99% purity. Over-all uniformity in thickness was better than 1% for each absorber. The areal density t_0 for each absorber was determined by dividing the weight of each disk by its precisely measured area.

A source of the 77.3-keV gold γ rays was prepared by activating one of several 200-mg platinum metal disks (enriched in Pt^{196}) in the Oak Ridge National Laboratory Research Reactor for 24 h. Neutron capture by Pt^{196} produces Pt^{197}, which β^- decays with a 20-h half-life[14] through the 77.3-keV first excited state of Au^{197}. The initial intensity of the 77.3-keV γ rays from a platinum source was typically on the order of 1 Ci.

The transmitted intensity from the platinum source through a gold absorber was measured by a Ge(Li) counter. A single-channel pulse-height analyzer was used to select pulses resulting from 77.3-keV γ rays and some background radiation. It is this single-channel selected transmission which was recorded by the multichannel analyzer as a function of Doppler velocity, and which is described by Eq. (1). The background radiation mentioned here was due in part to x rays produced by the activated isotopes of platinum in the source. The half-life of the Pt^{197} isotope is generally shorter than the half-lives of the other activated platinum isotopes. Therefore, the intensity of the 77.3-keV γ rays relative to the background intensity decreased with time during an experiment. This type of source behavior is accounted for in Eq. (1).

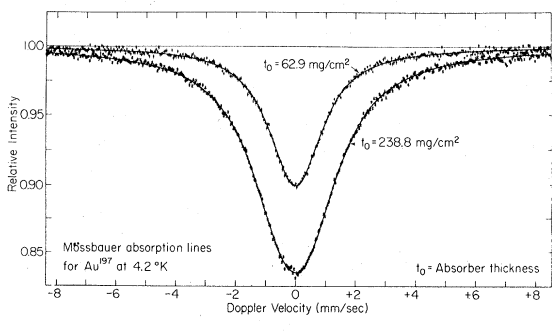

FIG. 1. Mössbauer absorption spectra for a thin and a thick gold absorber at 4.2 °K. An iterative scheme has been used to fit Eq. (1) to these spectra, from which the natural linewidth for the 77.3-keV state has been determined to be $\Gamma_0 = 0.923 \pm 0.006$ mm/sec. The solid curves represent the final fits to the data and are typical for the work presented here. Zero velocity has been shifted in this figure to the center of the gold absorption lines.

TABLE I. Summary of determinations of the natural linewidth Γ_0 or of the half-life $T_{1/2}$ for the 77.3-keV γ-ray transition in Au^{197}.

Type of measurement	Year of Ref.[a]	Γ_0 (mm/sec)	$T_{1/2}$ (nsec)
Coin.[b]	1955[c]	0.93 ±0.10	1.90 ±0.20
Möss.[d]	1963[e]	0.80 ±0.08	2.21 ±0.23
Möss.	1963[f]	0.92 ±0.10	1.93 ±0.21
Coin.	1968[g]	0.907±0.028	1.95 ±0.06
Möss.	1968[h]	0.935±0.007	1.892±0.014
Möss.	1968[i]	0.937±0.011	1.888±0.022
Möss.	This work[j]	0.923±0.006	1.917±0.012

[a]The earliest Mössbauer determination of Γ_0 can be found in Ref. 15.

[b]Coin. indicates that $T_{1/2}$ has been determined using delayed-coincidence techniques. Γ_0 has been obtained from $T_{1/2}$ using the relation $\Gamma_0 T_{1/2} = \hbar c \ln 2 / E_\gamma$, where $E_\gamma = 77.3$ keV.

[c]A. W. Sunyar, Phys. Rev. 98, 653 (1955).

[d]Möss. indicates that Γ_0 has been determined using Mössbauer techniques. $T_{1/2}$ has been obtained from Γ_0 using the above relation.

[e]Reference 16.

[f]Reference 17.

[g]M. T. R. Rao, V. V. Ramamurty, and V. Lakshminarayana, Indian J. Phys. 42, 709 (1968).

[h]P. Steiner, E. Gerdau, W. Hautsch, and D. Steenken, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland, Amsterdam, 1968), p. 364; Z. Physik 221, 281 (1969).

[i]Reference 18.

[j]This determination of Γ_0 also briefly reported by J. W. Burton, L. D. Roberts, and J. O. Thomson, Bull. Am. Phys. Soc. 13, 250 (1968).

V. EXPERIMENTAL RESULTS

The value of the natural linewidth for the 77.3-keV transition in Au^{197} has been redetermined because of its use in the thick-absorber line-shape analysis. An iterative scheme was used in least-squares fitting Eq. (1) to spectra for thin and thick gold absorbers (62.9 and 238.8 mg/cm²). These measurements were obtained with the absorbers at 4.2 °K. The two spectra with their final fits, which are typical of the work presented here, are shown in Fig. 1. The iterative procedure was started by approximating the thick-absorber spectrum using an assumed Γ_0. This gave an initial value for T_A. A better value for Γ_0 was then obtained by fitting the thin-absorber spectrum using the previously determined thick-absorber T_A reduced by the ratio of the t_0's. Iteration was continued until convergence in the values of Γ_0 and the thick-absorber T_A was obtained. The natural linewidth determined in this way is $\Gamma_0 = 0.923 \pm 0.006$ mm/sec. This corresponds to a half-life for the 77.3-keV state of 1.917 ± 0.012 nsec. Good agreement between this value and other values determined using both Mössbauer and coincidence techniques can be seen in Table I.

TABLE II. Values of $T_A(T)$, $f(T)/(1+\alpha)$, and $f(T)$ for pure gold determined from line-shape analysis on absorption spectra for thick gold absorbers. Values of $f(T)$ have been deduced using $\alpha = 4.30$.

Absorber temperature T (°K)	$T_A(T)$	$10^{+2} f(T)/(1+\alpha)$	$f(T)$
4.2	11.01±0.08	3.573±0.026	0.1894±0.0014
4.2	11.08±0.10	3.598±0.034	0.1907±0.0018
4.2	10.88±0.11	3.532±0.036	0.1872±0.0019
4.2	10.98±0.12	3.563±0.040	0.1888±0.0021
6.0	10.80±0.10	3.506±0.032	0.1858±0.0017
8.0	10.67±0.10	3.465±0.032	0.1836±0.0017
10.0	10.48±0.09	3.403±0.031	0.1804±0.0016
15.0	9.84±0.11	3.193±0.034	0.1692±0.0018
20.0	9.25±0.09	3.002±0.028	0.1591±0.0015
25.0	8.60±0.08	2.792±0.025	0.1480±0.0013
25.0	8.42±0.08	2.733±0.024	0.1448±0.0013
30.0	7.44±0.07	2.416±0.022	0.1280±0.0012
30.0	7.51±0.07	2.438±0.023	0.1292±0.0012
40.0	5.72±0.06	1.856±0.020	0.0984±0.0011
40.0[a]	11.51±0.10	1.871±0.017	0.0982±0.0009
49.8	4.29±0.05	1.394±0.017	0.0739±0.0009
50.0[a]	8.58±0.08	1.394±0.014	0.0739±0.0007
60.0[a]	6.16±0.09	1.001±0.015	0.0531±0.0008
79.8[a]	2.90±0.07	0.472±0.011	0.0250±0.0006
100.1[a]	1.12±0.08	0.181±0.013	0.0096±0.0007

[a]An absorber with $t_0 = 984.3$ mg of gold/cm^2 has been used at these temperatures. An absorber with $t_0 = 492.7$ mg of gold/cm^2 has been used at the other temperatures.

Values of $T_A(T)$ and $f(T)/(1+\alpha)$ which have been obtained from thick-absorber line-shape measurements are listed in Table II. Absorbers with thicknesses of 492.7 and 984.3 mg/cm^2 were used with the thicker absorber employed at the higher absorber temperatures. Fits of Eq. (1) to the measured thick-absorber line shapes were obtained using $\Gamma_0 = 0.923$ mm/sec. The total errors of the $T_A(T)$ and $f(T)/(1+\alpha)$ values have two principal contributions: (a) from the fitting of Eq. (1) to the line-shape data and (b) from the error in Γ_0. The errors quoted in Table II include only the (a) contribution and are appropriate to relative values of $T_A(T)$ and $f(T)/(1+\alpha)$. These errors represent about a 1% precision in the relative values of $f(T)/(1+\alpha)$ except at the higher absorber temperatures. The total errors including (a) and (b) contributions are approximately double the errors quoted in Table II.

VI. INTERNAL-CONVERSION COEFFICIENT

Deduction of absorber recoilless fractions from our data requires knowledge of the internal-conversion coefficient α of the 77.3-keV state of Au^{197}. Two independent estimates of α are discussed in this section.

A. α from Conversion-Electron Intensities

The γ rays resulting from the 77.3-keV transition are a mixture of $E2$ and $M1$ intensities.[19] Estimates of $F = E2/(E2+M1)$, the fraction of $E2$ radiation, and of α can be obtained from measurements of conversion-electron intensities used together with theoretical internal-conversion coefficients (ICC's). An estimate of this type by Shirley *et al.*[20] in 1961, giving $\alpha = 3.96 \pm 0.14$, has been used to interpret previous gold Mössbauer work. Since additional conversion data for the 77.3-keV state and newer theoretical ICC calculations have become available, we have redetermined F and α.

Using the theoretical L-subshell ICC's of Hager and Seltzer[21] (HS) and the conversion-intensity ratios L_{II}/L_I and L_{III}/L_I from the measurements of van Heerden *et al.*,[22] Jung and Svedberg,[23] and Bäcklin and Malmskog,[24] we have determined an average value of $F = 0.108 \pm 0.006$. The error on F results from the experimental errors reported for the measured conversion-intensity ratios. Since no experimental errors were reported, corresponding intensity data from earlier measurements[19,25] have not been used in the above determination of F, although these earlier data lead to values of F which are in good agreement with that above. From a similar analysis by Günther[26] using all of the available intensity data and the HS tables, an average value of F has been determined which is in excellent agreement with the above value.

The L- and M-shell contributions to α have been calculated using the HS tables and $F = 0.108 \pm 0.006$. The contribution to α from the $N+O+\cdots$ shells was approximated using this F and the theoretical ICC tables of Dragoun *et al.*[27] In this way, we have determined $\alpha = 4.23 \pm 0.09$. The error on α results primarily from the indicated error on F. Also included in this error is a 15% uncertainty in the theoretical ICC's for the $N+O+\cdots$ shells, as suggested by Dragoun *et al.*[27] No uncertainty in the HS tables has been estimated or included in this calculation of F and α.

B. α from Predicted f Values

The recoilless fraction can be written as

$$f(T) = \exp\{-(4\pi^2/\lambda^2)\langle x^2\rangle_T\}, \quad (4)$$

where λ is the wavelength of the resonance γ ray whose energy is E_γ, and $\langle x^2\rangle_T$ is the mean-square displacement of the absorbing atom in its host lattice along the direction of the incident γ ray. For a cubic monatomic lattice that is harmonically bound, the average $\langle x^2\rangle_T$ in Eq. (4) can be obtained in terms of a normalized phonon frequency distribution $g(\omega)$ such that $f(T)$ becomes

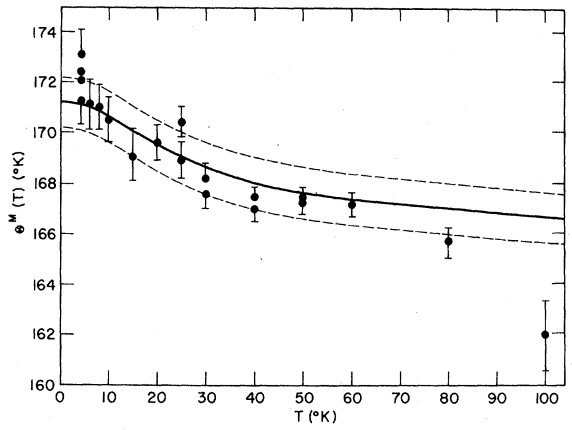

FIG. 2. Mössbauer effective Debe temperature $\Theta^M(T)$ for metallic gold versus T. The solid curve is an estimate of $\Theta^M(T)$ from a quasiharmonic analysis by Skelton and Feldman (Ref. 28) of gold thermodynamic data. The dashed curves represent the uncertainty in this estimate. The individual points are values obtained from our $f(T)/(1+\alpha)$ data if $\alpha = 4.37$ is assumed for the internal-conversion coefficient.

$$f(T) = \exp\left[-\frac{2R}{\hbar} \int_0^{\omega_m} \left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right) \frac{g(\omega)}{\omega}\, d\omega \right] . \tag{5}$$

Here $R = E_\gamma^2 / 2mc^2$ is the free-atom recoil energy and m is the atomic mass. ω_m is a cutoff frequency and $\beta = 1/kT$. Approximating $g(\omega)$ by a Debye frequency distribution with a cutoff frequency proportional to a Mössbauer effective Debye temperature $\Theta^M(T)$, one may obtain

$$f(T) = \exp\left\{ -\frac{3R}{2k\Theta^M(T)} \times \left[1 + 4\left(\frac{T}{\Theta^M(T)} \right)^2 \int_0^{\Theta^M(T)/T} \frac{x\,dx}{e^x - 1} \right] \right\} . \tag{6}$$

Skelton and Feldman[28] (SF) have recently estimated $\Theta^M(T)$ for metallic gold in the temperature range $0 \leq T \leq 120$ °K. This estimate is based on a quasiharmonic analysis of thermodynamic data from which moments of the gold frequency distribution have been obtained. Recoilless fractions for gold can be predicted from the results of SF and Eq. (6). These predicted recoilless fractions have been least-squares fitted to our $f(T)/(1+\alpha)$ data, excluding our 100 °K measurement, to obtain $\alpha = 4.37 \pm 0.10$. SF have similarly determined $\alpha \approx 4.4$ using our data. In Fig. 2 we have plotted $\Theta^M(T)$ estimated by SF and values of $\Theta^M(T)$ that can be determined from our data after reduction with $\alpha = 4.37$. Except at 100 °K, good agreement is obtained. It is expected that the disagreement at 100 °K is due to anharmonic effects not accounted for in the quasiharmonic approximation used by SF.

VII. DISCUSSION AND CONCLUSIONS

The two values for α obtained in Sec. VI, 4.23 ± 0.09 and 4.37 ± 0.10, agree within the estimated errors. This agreement is significant because of the wide variety of information used in making these independent determinations. It has been suggested that the Hager-Seltzer ICC tables, used in Sec. VI A to estimate α, may be accurate to 5% or better from comparison with experiment.[26,29] We note that the above agreement between the two determinations for α is within 3%. Because of this agreement, we choose a value for the internal-conversion coefficient of the 77.3-keV transition in Au^{197} to be $\alpha = 4.30$, which is an average of the results of Secs. VI A and VI B.

Values of the internal-conversion coefficient for the 99-keV Mössbauer state in Pt^{195} which have been determined from information[30–32] similar to that used in Sec. VI are also found to be in agreement.

We have reduced our thick-absorber data for $f(T)/(1+\alpha)$, assuming $\alpha = 4.30$, to obtain the values of $f(T)$ for metallic gold listed in Table II. These recoilless fraction values are plotted in Fig. 3 along with the $f(T)/(1+\alpha)$ data. The recoilless fraction for pure gold determined in this way varies from $f(4.2\,°\text{K}) = 0.189 \pm 0.001$ (an average of the four measurements given in Table II) to $f(100\,°\text{K}) = 0.0096 \pm 0.0007$. The errors on these f values represent the statistical errors quoted for the $f(T)/(1+\alpha)$ data in Table II. These errors give the precision associated with the relative values of $f(T)$ for gold. The errors associated with the absolute values of

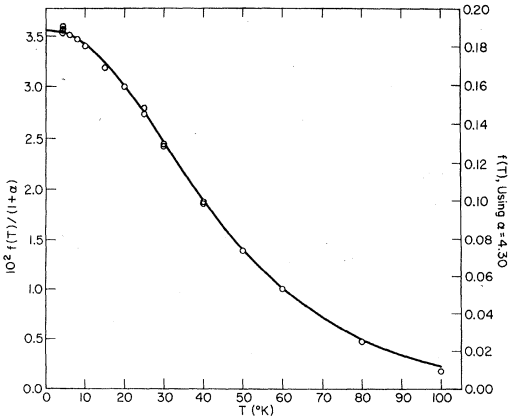

FIG. 3. Values of $f(T)/(1+\alpha)$ and of $f(T)$ for metallic gold as a function of absorber temperature T. The recoilless fractions have been deduced using $\alpha = 4.30$. The solid curve represents a best fit to our $f(T)/(1+\alpha)$ data using $f(T)$ as predicted from the results of Skelton and Feldman (Ref. 28) and $\alpha = 4.37$.

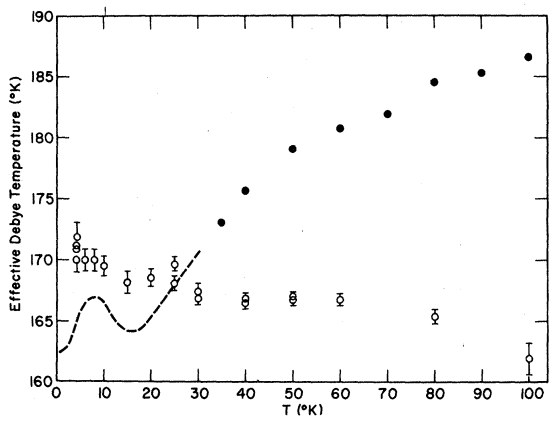

FIG. 4. Effective Debye temperatures for metallic gold, $\Theta^C(T)$ from specific-heat measurements and $\Theta^M(T)$ from our recoilless-fraction determinations, as a function of temperature. Dashed curve represents $\Theta^C(T)$ from measurements of Martin (Refs. 9 and 35). Closed circles represent $\Theta^C(T)$ from measurements of Geballe and Giauque (Ref. 36). Open circles represent $\Theta^M(T)$ determined from our $f(T)$ values which were obtained with $\alpha = 4.30$.

$f(T)$, however, may be several percent larger because of uncertainties in the values for α and for the natural linewidth Γ_0.

Early determinations of $f(T)$ have been made for metallic gold[15–17, 20, 33] at only a few temperatures and have larger associated errors than do the determinations of the present work. The recoilless fraction has also been obtained for gold microcrystals at several temperatures.[34] Recently, Ohlwiler[18] has obtained values of $f(T)$ for pure gold in the temperature range $4.2 \leq T \leq 100$ °K from linewidth measurements. The quoted precision of these $f(T)$ determinations is comparable to the results given here. A comparison of our $f(T)$ values with Ohlwiler's shows our values to be systematically higher and to have a smaller associated scatter. Our higher values appear to be due to our use of a somewhat larger estimate for α, a smaller value for Γ_0, and a more realistic line-shape description as given by Eq. (1) in the interpretation of our line-shape data.

In Fig. 4, we contrast $\Theta^M(T)$ determined from our gold $f(T)$ values, deduced using $\alpha = 4.30$, and $\Theta^C(T)$ for gold determined from specific-heat measurements of Martin[9, 35] and of Geballe and Giauque.[36] Over the temperature range $4.2 \leq T \leq 100$ °K, $\Theta^M(T)$ is seen to be much less temperature dependent than is $\Theta^C(T)$. The different behaviors of $\Theta^M(T)$ and $\Theta^C(T)$ occur because the recoilless fraction and the lattice specific heat are determined by quite different weighted averages over the frequency distribution $g(\omega)$.[37] A similar contrast is seen in the behaviors of $\Theta^M(T)$ and $\Theta^C(T)$ as determined from measurements on platinum.[30, 38] The low-temperature behavior of $\Theta^C(T)$ for gold is unusual or anomalous because, with increasing T, $\Theta^C(T)$ initially rises from $\Theta^C(0\,°K)$ to a maximum value at ≈ 8 °K. Our experimental values of $\Theta^M(T)$ for gold in Fig. 4, however, show little or no evidence of this anomalous behavior in the low-temperature region of our measurements.

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[1]Preliminary results reported by D. J. Erickson, L. D. Roberts, J. O. Thomson, and J. W. Burton, Bull. Am. Phys. Soc. 15, 180 (1970).

[2]W. A. Steyert and R. D. Taylor, Phys. Rev. 134, A716 (1964).

[3]R. M. Housley and J. G. Dash, Phys. Rev. 136, A464 (1964).

[4]R. H. Nussbaum, D. G. Howard, W. L. Nees, and C. F. Steen, Phys. Rev. 173, 653 (1968).

[5]R. M. Housley, N. E. Erickson, and J. G. Dash, Nucl. Instr. Methods 27, 29 (1964).

[6]J. G. Dash, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1965), Vol. I, p. 107.

[7]Values of $f(T)/(1+\alpha)$ have been determined for Au^{197} in ordered and disordered states of polycrystalline Cu_3Au in the temperature range $4.2 \leq T \leq 100$ °K. A larger recoilless fraction is found for Au^{197} in the more highly ordered state of Cu_3Au. Preliminary results have been reported by D. J. Erickson and L. D. Roberts, Bull. Am. Phys. Soc. 15, 1359 (1970).

[8]D. L. Martin, Phys. Rev. Letters 12, 723 (1964).

[9]D. L. Martin, Phys. Rev. 141, 576 (1966).

[10]H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1962), p. 7.

[11]S. Margulies and J. R. Ehrman, Nucl. Instr. Methods 12, 131 (1961).
[12]L. D. Roberts, D. O. Patterson, J. O. Thomson, and R. P. Levey, Phys. Rev. 179, 656 (1969).
[13]D. O. Patterson, J. O. Thomson, P. G. Huray, and L. D. Roberts, Phys. Rev. B 2, 2440 (1970).
[14]M. Bresesti and J. C. Roy, Can. J. Chem. 38, 194 (1960).
[15]D. Nagle, P. P. Craig, J. G. Dash, and R. R. Reiswig, Phys. Rev. Letters 4, 237 (1960).
[16]H. J. Andrä, C. M. H. Hashmi, P. Kienle, and F. W. Stanek, Z. Naturforsch. 18A, 687 (1963).
[17]L. D. Roberts and J. O. Thomson, Phys. Rev. 129, 664 (1963).
[18]R. W. Ohlwiler, dissertation, University of California, Davis, 1968 (unpublished).
[19]J. W. Mihelich and A. de-Shalit, Phys. Rev. 91, 78 (1953).
[20]D. A. Shirley, M. Kaplan, and P. Axel, Phys. Rev. 123, 816 (1961).
[21]R. S. Hager and E. C. Seltzer, Nucl. Data A4, (1968).
[22]I. J. van Heerden, D. Reitmann, and H. Schneider, Nuovo Cimento 11, 167 (1959).
[23]B. Jung and J. Svedberg, Arkiv Fysik 19, 429 (1961).
[24]A. Bäcklin and S. G. Malmskog, Arkiv Fysik 34, 59 (1967).
[25]O. Huber, J. Halter, R. Joly, D. Maeder, and J. Brunner, Helv. Phys. Acta 26, 591 (1953); R. Joly, J. Brunner, J. Halter, and O. Huber, *ibid.* 28, 403 (1955).
[26]C. Günther (private communication).
[27]O. Dragoun, Z. Plajner, and F. Schmutzler (unpublished); we are indebted to O. Dragoun (private communication) for generously supplying us with the appropriate ICC's for $Z=79$ and $E_\gamma=77.3$ keV from these tables prior to publication.
[28]E. F. Skelton and J. L. Feldman (unpublished).
[29]J. C. Manthuruthil and J. H. Hamilton, in Proceedings of the International Conference on Radioactivity in Nuclear Spectroscopy, Vanderbilt University, Nashville, Tenn., 1969 (unpublished).
[30]J. R. Harris, N. Benczer-Koller, and G. M. Rothberg, Phys. Rev. 137, A1101, (1965).
[31]J. L. Feldman and G. K. Horton, Phys. Rev. 137, A1106 (1965).
[32]J. R. Harris, G. M. Rothberg, and N. Benczer-Koller, Phys. Rev. 138, B554 (1965).
[33]J. Speth and F. W. Stanek, Z. Naturforsch. 20A, 1175 (1965).
[34]J. W. Marshall and R. M. Wilenzick, Phys. Rev. Letters 16, 219 (1966).
[35]D. L. Martin, Phys. Rev. 170, 650 (1968).
[36]T. H. Geballe and W. F. Giauque, J. Am. Chem. Soc. 74, 2368 (1952).
[37]The different averages over a frequency distribution which determine the recoilless fraction and the lattice specific heat are discussed by R. H. Nussbaum, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1966), Vol. II, p. 3.
[38]G. E. Shoemake and J. A. Rayne, Phys. Letters 26A, 222 (1968).

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Electronic Structure and Spectrum of the NiF_6^{-4} Cluster: Results of Calculations Based on Self-Consistent-Field Models*

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Restricted and unrestricted Hartree-Fock molecular-orbital self-consistent-field calculations were performed on the cluster NiF_6^{-4} with a fixed internuclear distance appropriate to $KNiF_3$. A slightly extended multicenter atomic-orbital basis was used. In contrast to the approach of earlier calculations which sought to describe $10Dq$ as a single electron promotion between t_{2g} and e_g antibonding (LCAO) molecular orbitals, we obtained the spectra as the difference in energy between various many-electron open-shell states. The results obtained with limited configuration interaction are in good agreement with the five observed optical absorption bands. We find that the earlier orbital picture can be approximately maintained only if the covalency parameters are obtained from the *open-shell* orbitals of excited states, which are solutions of the Hartree-Fock-Roothaan Hamiltonians. In these orbitals we find considerable σ bonding and a smaller π bonding, significant fluoride s-p hybridization, and a small expansion of the $3d$ orbitals which is greater in the t_{2g} than in the e_g orbitals. Allowing for spin-polarization correlation in the unrestricted calculations, however, adds important contributions to transferred hyperfine interactions and neutron form factors.

I. INTRODUCTION

Continued interest in the optical, magnetic, and structural properties of transition-metal compounds arising from the occurrence of unfilled shells associated with the metal-ion $3d$ electrons has led to a wide variety of attempts at theoretical explanation. Recent theoretical emphasis has concentrated on clusters containing the transition-metal ion surrounded by its nearest-neighbor anions or ligands