Solid-State and Nuclear Results from a Measurement of the Pressure Dependence of the Energy of the Resonance Gamma Ray of ^{197}Au†

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Metallic gold has been subjected to a sequence of pressures in the range from 0 to 70.6 kbar at a temperature of 4.2°K, and the change of the energy of the ^{197}Au resonance γ ray with pressure has been measured. The measurements were made by the Mössbauer method. The result for dE_γ/dP is in good agreement with an earlier prediction for this quantity based on a correlation of the Mössbauer isomer shift with residual electrical resistance for a series of dilute gold alloys. We have used the Wigner-Seitz approximation to describe the gold 6*s* band, and this wave function has been calculated in a relativistic Hartree approximation. Within this treatment we find that the gold nucleus increases in size when excited, with $\Delta r/r \cong +1.5\times10^{-4}$. A brief comment is made on the bearing which these results have on the charge and screening of gold atoms in dilute gold alloys.

I. INTRODUCTION

INFORMATION about the electric charge which is associated with an atom in a solid may be obtained for a number of elements through the use of the exceedingly precise γ-ray energy measurements which are made possible by the Mössbauer effect.[1] The electronic charge on an atom penetrates the nucleus in some degree and produces a slight displacement in the energy of each of the nuclear energy levels. In a first-order perturbation-theory treatment,[2] this displacement is proportional to the square of the radial-wave function $|\psi(r_0)|^2$ at the nuclear radius r_0. [See Eq. (7) and the text following this.] Thus, when the constant of proportionality has been determined, a measurement of the displacement in the energy of the resonance γ ray of an isotope due to its chemical environment can give a sensitive measurement of the electron charge density near the nucleus which is associated with that chemical environment. In Mössbauer-effect measurements one actually measures the difference in this resonance γ-ray energy displacement between the source and absorber of the γ rays. This difference[3] is usually referred to as the isomer shift ΔE. Shirley *et al.*[4] and the authors[5,6] have previously reported measurements of ΔE for metallic gold and for a number of gold alloys and compounds. Some of these results have been interpreted[4–6] to give a value for the constant of proportionality between ΔE and $|\psi(r_0)|^2$. The present paper gives further information about the dependency of ΔE on $|\psi(r_0)|^2$ for ^{197}Au. These new results have been obtained by high-pressure Mössbauer-effect measurements on metallic gold at a temperature of 4.2°K.

A number of high-pressure Mössbauer-effect measurements have been made previously, for example by Pound *et al.*[7] for iron, by Drickamer *et al.*[8] for iron and iron alloys, by Panyushkin *et al.*[9] for tin, and by Jura *et al.*[10] for iron alloyed in nickel. As far as we are aware our work is the only high-pressure Mössbauer-effect study which has been made for gold and is the only high-pressure Mössbauer effect work which has been done at liquid-helium temperatures.[11] Several brief reports of this work have been given previously.[12,13]

When gold is compressed, the electron charge density within the gold nucleus is modified, and correspondingly

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[1] H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1963).

[2] G. Breit, Rev. Mod. Phys. **30**, 507 (1958).

[3] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[4] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964); P. H. Barrett, R. W. Grant, M. Kaplan, and D. A. Shirley, J. Chem. Phys. **39**, 1035 (1963).

[5] Louis D. Roberts and J. O. Thomson, Phys. Rev. **129**, 664 (1963).

[6] Louis D. Roberts, Richard L. Becker, F. E. Obenshain, and J. O. Thomson, Phys. Rev. **137**, A895 (1965).

[7] R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters **7**, 405 (1961).

[8] R. Ingalls, H. G. Drickamer, and G. DePasquali, Phys. Rev. **155**, 165 (1967).

[9] V. N. Panyushkin and F. F. Voronov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **2**, 153 (1965) [English transl.: Soviet Phys.—JETP Letters **2**, 97 (1965)].

[10] D. L. Raimondi and G. Jura, J. Appl. Phys. **38** (5), 2133 (1967).

[11] D. O. Patterson, thesis, University of Tennessee, 1966 (unpublished); D. O. Patterson, Louis D. Roberts, J. O. Thomson, and R. P. Levey, Oak Ridge National Laboratory Report No. TM-1685, 1967 (unpublished).

[12] Louis D. Roberts, J. O. Thomson, D. O. Patterson, and R. P. Levey, Bull. Am. Phys. Soc. **11**, 49 (1966).

[13] Louis D. Roberts, D. O. Patterson, J. O. Thomson, and R. P. Levey, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967). In this earlier report, there is a small calibration error in the pressure scale. This has been corrected in the present paper.

there will be a change $\Delta E(P)=E_\gamma(P)-E_\gamma(0)$ in the resonance γ-ray transition energy. Here $E_\gamma(0)$ (approximately 77.345 keV) is the energy of the resonance γ ray for metallic gold at zero pressure, and $E_\gamma(P)$ is this energy when the gold has been compressed under a pressure P. In the interpretation of our measurements, as will be discussed below, we will use the first-order perturbation-theory result[2] that

$$\Delta E(P)=\lambda n|\psi_0(r_0)|^2 \times[|\psi_P(r_0)|^2-|\psi_0(r_0)|^2]/|\psi_0(r_0)|^2, \quad (1)$$

where λ is a calculable constant,[1,2] n is a factor depending only on nuclear parameters, and $|\psi_P(r_0)|^2$ and $|\psi_0(r_0)|^2$ describe the electron charge density within the nucleus when the gold is under a pressure P, and at zero pressure, respectively.

A complete interpretation of our measurements of $\Delta E(P)$ can only be given if one has a knowledge of the way the Au band structure, and thus $|\psi_P(r_0)|^2$, changes with the atomic volume of the gold when the sample is compressed. In that the band structure of gold has not yet been calculated, we present here an approximate interpretation of our measurements in terms of the Wigner-Seitz model. To obtain $|\psi_P(r_0)|^2$ in this approximation, a numerical solution of the Dirac equation for gold in the Hartree self-consistent field approximation with Wigner-Seitz boundary conditions has been obtained. In this calculation, which is described in an earlier paper,[14] the effect of a compression of the atom on the wave functions is described through a change in the radius of the Wigner-Seitz cell, R. We note that Ingalls,[15] and Ingalls, Drickamer, and DePasquali[8] have recently used an approximate band-theory calculation to describe high-pressure Mössbauer studies on iron and on iron alloys.

In the Wigner-Seitz model, the Bloch wave function $U_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ is approximated by $U_0(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$, where for gold $U_0\cong U_{\mathbf{k}}$ (with $\mathbf{k}=0$) is for a $6s$ state. Here $|\psi(r_0)|^2$ is assumed to be equal to $|U_0(r_0)|^2$, where the latter function has been normalized to one electron per Wigner-Seitz cell. In the Wigner-Seitz model, because the $\vec{k}$ dependence of U is neglected, the amount of $6s$ character in the gold valence band is overestimated, and the logarithmic derivative of $|\psi_P(r_0)|^2$ with respect to R^{-3}, Eq. (5) below, may also be appreciably in error. We regard our calculation of the isomer shift in terms of the Wigner-Seitz model, Eq. (7) below, as a step toward the full-band-theory treatment. A complete calculation of $|U_{\mathbf{k}}(r_0)|^2$ will be necessary to obtain a definitive treatment of the isomer shift and of our measurements, but the present Wigner-Seitz treatment may give a semiquantitative description of the electron charge density near the gold nucleus as a function of average metallic density. Some additional remarks relative to this are made below.

[14] T. Tucker, Louis D. Roberts, C. W. Nestor, Jr., T. A. Carlson, and F. B. Malik, Phys. Rev. **178**, 998 (1969).

[15] R. Ingalls, Phys. Rev. **155**, 157 (1967).

As was mentioned above, in an earlier paper[6] the sign and magnitude of this pressure dependence of the γ-ray energy $E_\gamma(P)$ were predicted. In terms of the Doppler velocity units natural to the Mössbauer-effect measurement, this dependence was given to terms linear in P as

$$v(P)=c\left[\frac{\Delta E(P)}{E_\gamma(0)}\right]=\frac{c\lambda n|\psi_0(r_0)|^2}{E_\gamma(0)}\left[\frac{|\psi_P(r_0)|^2}{|\psi_0(r_0)|^2}-1\right] \quad (2a)$$

$$=G\left[\frac{|\psi_P(r_0)|^2}{|\psi_0(r_0)|^2}-1\right]\text{ cm/sec} \quad (2b)$$

$$\cong 0.0005P\text{ cm/sec}, \quad (2c)$$

where c is the velocity of light, P is the pressure in kilobars, and $v(P)$ is the Doppler velocity equivalent to $\Delta E(P)$. It was a result of this earlier work that the quantity $G=c\lambda n|\psi_0(r_0)|^2/E_\gamma(0)$, Eq. (2b), has a value near $+0.8$ cm/sec. Shirley *et al.*[4] have given a larger value of $+1$ to $+2$ cm/sec and also $+1.5$ cm/sec from other considerations.

In giving the relation Eq. (2c), we tentatively assumed that $|\psi_P(r_0)|^2$ is proportional to the density of the bulk solid as a function of pressure,[16] i.e., that

$$[|\psi_P(r_0)|^2-|\psi_0(r_0)|^2]/|\psi_0(r_0)|^2\cong KP,$$

where K is the compressibility of metallic gold. Here $|\psi_P(r_0)|^2$ and thus $v(P)$ or $\Delta E(P)$ is obtained in a somewhat better approximation for gold through the use of the calculated atomic wave functions for gold referred to above.[14]

This earlier prediction[6] of $\Delta E(P)$ or alternatively of $v(P)$ given in Eqs. (2) was based on an experimental and theoretical investigation of the correlation to be expected between the energy E_γ(alloy) of the recoil-free γ ray emitted by ^{197}Au in a dilute alloy and the residual electrical resistivity per at.% $\Delta R/X$ which the gold atoms introduced into the alloy. The theoretical model which was used for this gives a description of the isomer shift as an aspect of the screening of the gold in a dilute alloy[17] and is an extension of earlier descriptions[18] of the Knight shift in dilute alloys in terms of a screening model by Daniel and by Kohn and Vosko.

A good correlation was found between ΔE(alloy) $=E_\gamma$(alloy)$-E_\gamma(0)$ and $\Delta R/X$ for dilute alloys of gold in copper, silver, palladium, and platinum under the principal assumptions that (a) for a gold atom in the alloy, conduction-band electrons provide the screening

[16] A similar model has been used previously, for example, for iron by H. G. Drickamer, R. L. Ingalls, and C. J. Coston, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 314.

[17] V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. **47**, 80 (1964) [English transl.: Soviet Phys.—JETP **20**, 55 (1965)]. These authors suggest that the correlation which they have observed for dilute tin alloys between the tin isomer shift and the force constant for the binding of the tin in the host may be explainable in terms of a screening model.

[18] E. Daniel, Phys. Chem. Solids **10**, 174 (1959); W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

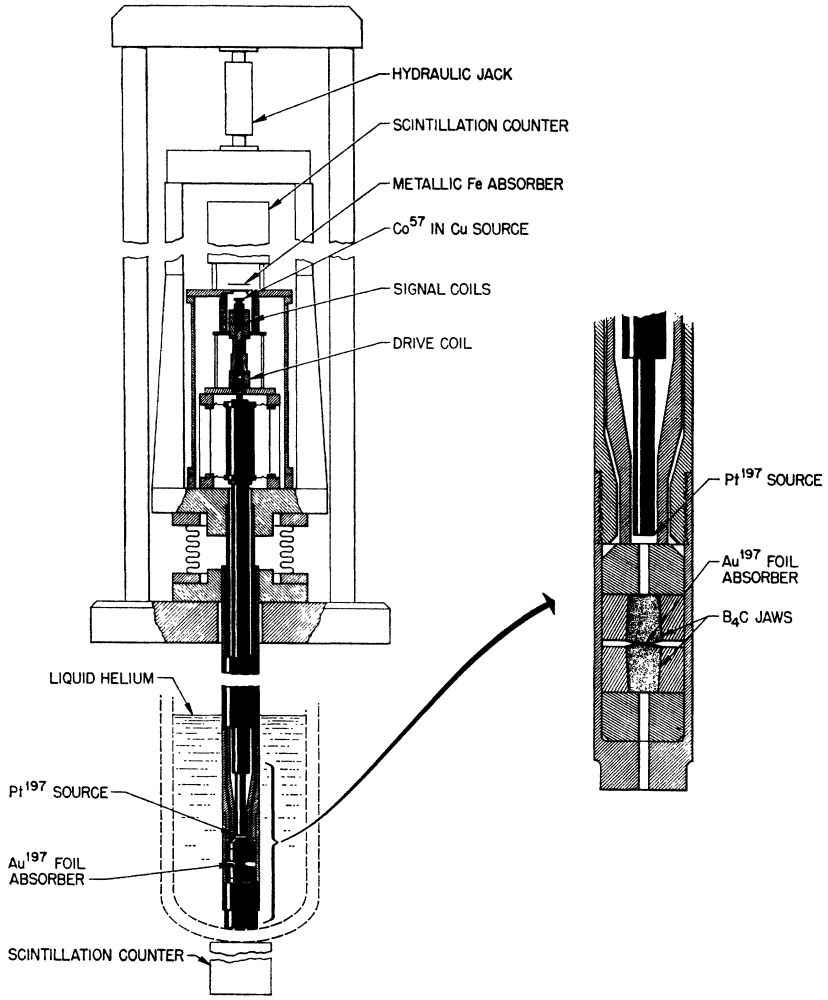

FIG. 1. Apparatus which was used for making Mössbauer-effect measurements at high pressures and at liquid-helium temperatures. A ^{197}Pt source is mounted at the lower end of the armature of the transducer and a ^{57}Co in Cu source at the upper end. This makes it possible to measure the pressure dependence of the resonance γ ray of gold relative to the 6-line hyperfine structure spectrum of the resonance γ ray of ^{57}Fe in metallic iron. The parts of the apparatus, other than the jaws, which may be under a high tensile stress were fabricated from the maraging steel Vascomax 300. Each of the jaws of the press was fabricated by forcing a 1% oversize tapered plug of B_4C into a hardened Vascomax 300 steel ring. With this arrangement, the B_4C plugs have been loaded to approximately twice the compressive strength of an unsupported B_4C cylinder without failure. The B_4C jaws were used so that a high pressure could be applied to the gold sample with a minimum γ-ray attenuation. The question of the uniformity of the pressure is discussed in the text.

that is associated with the charge density at the gold nucleus, (b) that the gold presented an attractive potential to the conduction electron partial waves of zero orbital angular momentum (s partial waves), (c) that the s-band populations were 1.0, 1.0, 0.67, and 0.50 for Cu, Ag, Pd, and Pt. For all of these alloys, this correlation led to the conclusion that near the gold nucleus the gold atom became negatively charged compared to pure metallic gold. The value for the coefficient $G=c\lambda n|\psi_0(r_0)|^2/E_\gamma(0)\cong 0.8$ cm/sec given above was obtained from this correlation. Here we report a value for this coefficient G obtained through our high-pressure measurements and compare this with the value for G obtained through the above screening model correlation. As will be seen, the values for G obtained in these two ways are in agreement within the experimental errors.

It is convenient to break up the discussion of this high-pressure study into several sections. In Sec. II of this paper we will devote our attention to the several aspects of the high-pressure Mössbauer-effect measurements. In Sec. III we will compare these results with our earlier gold-alloy studies and will comment briefly on the relation of this work to screening in alloys dilute in gold. A brief discussion of the nuclear factor in Eq. (1) will be given. In an earlier paper,[14] the calculation of the gold Wigner-Seitz wave functions has been presented in detail.

II. HIGH-PRESSURE MÖSSBAUER-EFFECT MEASUREMENTS

The apparatus used for the high-pressure measurements is shown in Fig. 1. The source of the gold γ rays was prepared by activating approximately 0.2g of Pt enriched in ^{196}Pt in the Oak Ridge Research Reactor for 24 h. This source was mounted on a sine-wave transducer immediately above and coaxial with two Bridgman anvils fabricated from sintered boron carbide. These anvils were used to compress a gold absorber foil of 0.002 in. thickness over a circular area of 0.187 in. diam. These anvils have been loaded to $\sim$15 tons or to an average pressure over the 0.187-in.-diam area of

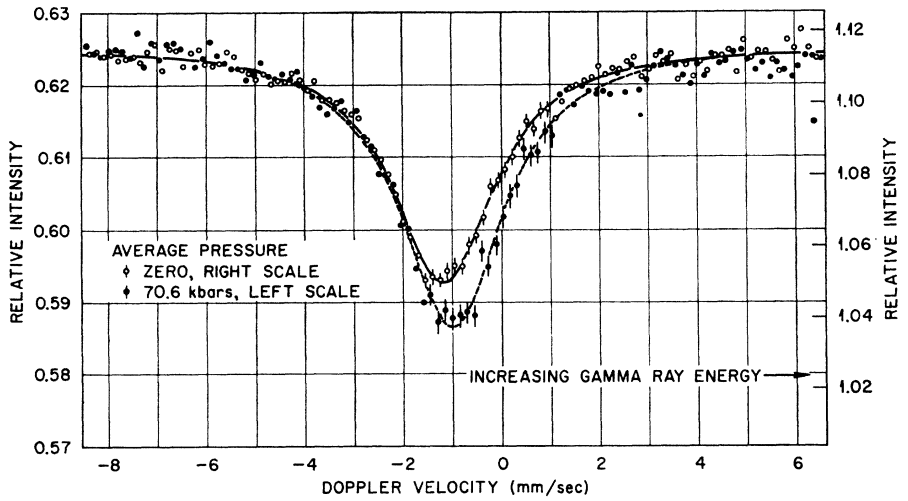

FIG. 2. Mössbauer spectrum for metallic gold at zero pressure and at an applied average pressure of 70.6 kbar. The energy of the resonance γ ray of ^{197}Au in metallic gold is shown to increase with pressure. The Lorentz curves passing through the experimental points have been fitted by a least squares procedure. The difference in relative intensity of the two curves is not of significance.

approximately 71 kbar at 4.2°K without failure. The collimated γ-ray beam was directed normally to the foil and in most of the measurements passed through a circular area 0.125 in. in diameter central to the compressed region. In one measurement at an applied average pressure of 55 kbar, the γ rays were permitted to pass through the entire area of gold of 0.187 in. diam which was under compression. In spite of the fact that the γ rays passed through a total thickness of B_4C of 4.4 cm, the source strength was sufficient to give a counting rate of 1.5×10^5 counts/min for the 0.125-in.-diam collimated beam using a NaI(Tl) counter. This intensity included resonance γ rays and an appreciable but undetermined fraction of unresolved x rays. A multichannel analyzer was used in a pulse-height mode in recording the Mössbauer-effect spectrum.

In making these measurements, a six-line Mössbauer spectrum of metallic Armco iron and the single-line ^{197}Au Mössbauer spectrum were taken with the ^{197}Pt and the ^{57}Co sources mounted respectively at the lower and upper ends of the armature of the sine-wave transducer (Fig. 1). For the iron spectrum the source and absorber were at room temperature (295°K) while for the gold spectrum they were at 4.2°K. The same basic electronics were simultaneously used in obtaining the gold and iron spectra and in routing the information about the two spectra to different memory banks of the multichannel analyzer. Thus our measurements of $v(P)$ for the ^{197}Au γ rays were made relative to or in direct comparison with the six γ-ray energies of the iron hfs spectrum which, of course, remained unchanged throughout the series of measurements. Our results for $v(P)$ are then very nearly independent of any slight drift in the gain of the electronic equipment, and it is felt that the error in the relative velocity calibration between different Mössbauer-effect measurements is of the order of 10^{-4} cm/sec. The calibration of our measurements is obtained by comparing the above 6-line iron spectra with the measurements made for metallic iron by Preston, Hanna, and Heberle.[19] The above measurement technique is also discussed in another paper.[20]

Figure 2 shows the observed spectrum of ^{197}Au at zero pressure and at an average pressure of 70.6 kbar. The shift of the line center of the gold resonance γ ray with compression is well resolved. The solid curves shown in the figure are Lorentz line shape functions which have been fitted by a least squares procedure[21] to the experimental points. Using this least-squares procedure, Lorentz lines have been fitted to the results of eight measurements made at five average pressures where the collimated γ-ray beam was 0.125 in. in diameter. As expected, the linewidth was found to be independent of pressure to within the experimental error of a few percent of the linewidth. This is discussed below. The line centers were located to within an error of 0.01 to 0.02 mm/sec. The points in Fig. 3, with their respective errors,[21] give the experimental results for $v(P_0)$ and $\Delta E(P_0)$ as a function of average pressure P_0. An estimate of the second-order Doppler shift as a function of pressure shows that for $0\leq P\leq 70.6$ kbar, the change of this shift with pressure is small compared to $\Delta E(P)$. This is also true for the high-pressure Mössbauer studies which have been made for iron.[8] No correction for this shift is included in the results presented here.

Usually one of the most important technical problems in high-pressure physics where Bridgman anvils are used is the determination of the pressure distribution between the anvils. This information is not essential, however, in the interpretation of the measurements shown in Fig. 3 because—to first order—the isomer shift is proportional

[19] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

[20] D. O. Patterson, P. G. Huray, J. O. Thomson, and Louis D. Roberts, Phys. Rev. (to be published).

[21] This least-squares code was developed by Gordon Czjzek of the Oak Ridge National Laboratory. The errors quoted are standard deviations and were calculated by the method described by P. Cziffra and M. J. Moravcsik, University of California Lawrence Radiation Laboratory Report No. UCRL-8523, 1958 (unpublished).

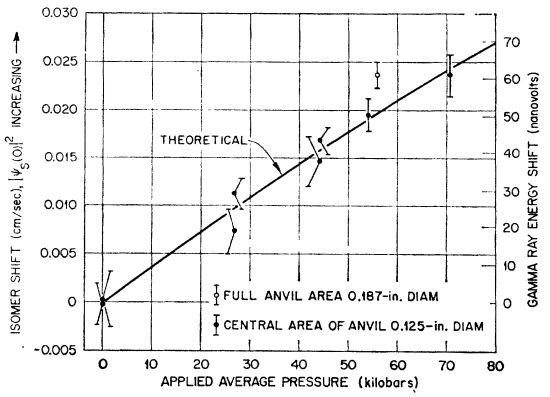

FIG. 3. The shift of the resonance γ-ray energy for gold with applied average pressure. The γ-ray energy increases with pressure by about 1 nV/kbar. The solid curve labeled theoretical represents a prediction of this pressure dependence of E_γ from an earlier study of the correlation of E_γ with the electrical resistance of alloys dilute in gold, Ref. 6. For this curve $g=0.68\pm0.1$ cm/sec. See Eqs. (2) and (10).

to the average applied pressure if this shift is small compared to the Mössbauer linewidth. This may be illustrated by the following simple calculation. We assume that the isomer shift $\Delta\epsilon$ of a given atom is proportional to the pressure P to which the atom is subjected, $\Delta\epsilon=\beta P$. Here, and in Eqs. (3) below, the unit of energy is $\frac{1}{2}\Gamma$, half of the natural width of the resonance. The sample is taken to have an area A and we define an average pressure $P_0=(1/A)\int_A P(a)da$. We also assume that the number of atoms subject to a given pressure is $N(P)$ with $N_0=\int_P N(P)dP$, where N_0 is the total number of atoms in the sample. Then the resonance cross section $\sigma(E,P)$ as a function of E and P is

$$\sigma(E,P)=N(P)\sigma_0/[(E-\beta P)^2+1]. \tag{3a}$$

If we write the pressure $P=P_0+p$ and assume that $\beta P\ll 1$, we obtain

$$\sigma(E,P_0,p)\cong\frac{N(P_0+p)\sigma_0}{1+(E-\beta P_0)^2}\times\left[1-\frac{(2\beta^2P_0-2\beta E)p+\beta^2p^2}{1+(E-\beta P_0)^2}\right], \tag{3b}$$

$$\sigma(E,P_0)=\int dp\,\sigma(E,P_0,p)=\frac{N_0\sigma_0}{1+(E-\beta P_0)^2}\times\left[1-\frac{(2\beta^2P_0-2\beta E)\langle p\rangle+\beta^2\langle p^2\rangle}{1+(E-\beta P_0)^2}\right], \tag{3c}$$

where

$$\langle p\rangle=N_0^{-1}\int dp\,pN(P_0+p)\cong 0$$

and

$$\langle p^2\rangle=N_0^{-1}\int dp\,p^2N(P_0+p)$$

is expected to be small. Here we have shown that for $\Delta E\ll\frac{1}{2}\Gamma$ the isomer shift is closely proportional to the average pressure P_0 and that the expected correction to the line shape is small.

Since $\Delta E(P_0)$ is related to the density of the compressed solid, the measurement of this quantity for different areas of the compressed solid can give information about the density and thus about the pressure distribution between the Bridgman anvils. At 55 kbar we have made a measurement of $\Delta E(P_0)$ over the entire compressed area 0.187 in. in diameter as well as over a central region 0.125 in. in diameter. The near agreement of $\Delta E(P_0)$ for these two measurements (Fig. 3) suggests that any effect of a nonuniformity of pressure over the compressed gold foil is only of the same magnitude as the statistical errors in these measurements. On the basis of the above considerations, we feel that our measurement of $\Delta E(P_0)$ is correct within about the statistical errors shown in Fig. 3. The measurements taken over the central region of the gold sample 0.125 in. in diameter are thought to be representative. Only these points are used in the following discussion, Sec. III, with the exception that the errors given for G and for the coefficient of $\Delta R^{-3}/R^{-3}$, below, are sufficiently large to embrace all of the measured points.

III. DISCUSSION

When pressure is applied to gold, the average electron density within the gold sample increases and this increase may be estimated from the compressibility and the applied pressure. Our measurements give information, not about the average electron density, however, but rather specifically about the electron charge density in the immediate vicinity of the gold nucleus. Thus, to interpret our measurements, Fig. 3, it is necessary to relate the electron density near the gold nucleus, as described by $|\psi_P(r_0)|^2$, to the average density of the metallic gold. As was mentioned above, we do this for the present in terms of a calculation of the relativistic electron wave functions for a gold atom with Wigner-Seitz boundary conditions, a calculation which is described in an earlier paper.[14]

In the solution of the Dirac equations only $s_{1/2}$ and $p_{1/2}$ states contribute appreciably to the charge density near the nucleus. For a point nucleus, and for values of the radius r in the range $0\leq r\leq r_0$, where r_0 is the radius of the nuclear surface, the calculated radial electron probability density $|\psi(r)|^2$ is described to within a few percent by the approximate form

$$r^2|\psi(r)|^2=C_{nj}(R)r^{2\gamma}, \tag{4}$$

where $\gamma=(1-\alpha^2Z^2)^{1/2}$, r is the distance from the origin, α is the fine structure constant and Z is the nuclear charge. The quantity $C_{nj}(R)$ characterizes this charge density as a function of R, the Wigner-Seitz cell radius, for states of principal quantum number n and angular momentum j. In an earlier paper,[14] we have given a more complete discussion of the calculated values for

the $C_{nj}(R)$. Here we note two useful conclusions obtained from these calculations. First, at or near the density of metallic gold ($R=2.998$ a.u.), the change of charge density at the nucleus with R is due almost entirely to the change of the $6s_{1/2}$ wave function with R. Only $C_{6s}(R)$ changes appreciably with R. The C_{nj} for the inner-shell electrons are very nearly independent of R for the region of importance in this measurement, $3.000 \geq R \geq 2.970$ a.u. This is a most helpful result for it indicates that, within the Wigner-Seitz model, our measurements may be interpreted simply in terms of the $6s$ electron shell of gold. The $5d$ wave functions will of course change as the sample is compressed and this will indirectly affect $C_{6s}(R)$ through screening. This is taken into account in that the gold wave functions have been calculated in the Hartree approximation.[14] A second result from the wave-function calculation is the quantitative one that $C_{6s}(3.000)=67.27$ a.u., and that

$$[d \ln C_{6s}(R)/d \ln R^{-3}]_{\mathrm{Au}}=0.86 \qquad (5)$$

over the range $2.970 \leq R \leq 3.000$. A subscript Au designates the fact that the derivative has been evaluated in this range of R—the range within which our high-pressure measurements were made.

In the Wigner-Seitz model the volume of the metal sample V is given by $\frac{1}{3}4\pi R^3 N$ where N is the number of atoms in the sample. Then, using Eqs. (4) and (5), we may write $|\psi(r_0)|^2 \propto V^{-0.86}$. Ingalls,[15] and Ingalls, Drickamer, and DePasquali[8] have given a value of -1.25 for iron for the corresponding exponent of V. In earlier work Drickamer *et al.*,[16] for example, and also we[6] have assumed that $|\psi(r_0)|^2$ scaled as V^{-1}. This would correspond to a value for the logarithmic derivative of $d \ln C(R)/d \ln R^{-3}=1$. Thus the Wigner-Seitz treatment we have used here leads to a modest correction to the simple scaling model[6,16] in the calculation of the isomer shift, Eq. (7).

The isomer shift $\Delta E(P)$, Eq. (1), may be written[2] in terms of $C_{6s}(R)$. If we suppose that the gold nucleus is a sphere of uniform charge density and of radius r_0, the potential felt by an electron will be

$$V(r)=-\frac{Z|e|}{2r_0}\left[\left(\frac{r}{r_0}\right)^2-3\right], \quad r \leq r_0$$
$$=+\frac{Z|e|}{r}, \quad r \geq r_0. \qquad (6)$$

Then, using first-order perturbation theory and Eq. (4), the isomer shift may be written

$$\Delta E=\frac{6}{(2\gamma+1)(2\gamma+3)}\left(\frac{Ze^2}{2a_0}\right) \times[C_{6s}(R_{\mathrm{Au}})r_0^{2\gamma}]\left(\frac{d \ln C_{6s}}{d \ln R^{-3}}\right)_{\mathrm{Au}}\left(\frac{\Delta r_0}{r_0}\right)\left(\frac{\Delta R^{-3}}{R^{-3}}\right), \qquad (7)$$

where a_0 is the Bohr radius and the quantity $C_{6s}(R_{\mathrm{Au}})r_0^{2\gamma}=r_0^2|\psi(r_0)|^2$ is in atomic units. In the above equation the effect of compression is given in terms of the change of R^{-3} or of the gold density with pressure. For small volume changes, $-\Delta R^{-3}/R^{-3}=\Delta V/V$, where V is the volume of the gold sample.

In Eq. (7), ΔE is given in terms of $|\psi(r_0)|^2$, the electron charge density at the nuclear surface. Frequently, in the calculation[1,2,14] of ΔE, $|\psi(r_0)|^2$ is given approximately in terms of $|\psi(0)|^2$. We prefer to use the result given in Eq. (7) because $|\psi(0)|^2$, Eq. (4), for a Dirac electron and a point nucleus is infinite. The subject has been discussed at some length in an earlier paper.[14]

No bulk modulus measurements have been made for gold in the liquid-helium temperature range but the elastic stiffness constants C_{11} and C_{12} have been measured in this temperature region. For 0°K, the values $C_{11}=2.016$ and $C_{12}=1.697$ in units of 10^{12} dyn/cm^2 have been given by Alers and Neighbours.[22] Using a model assumed by Slater[23] for the term quadratic in the pressure, we obtain

$$\frac{\Delta V}{V}=-\frac{3}{C_{11}+2C_{12}}P+\frac{2.51\times 3^2}{(C_{11}+2C_{12})^2}P^2$$
$$=-[5.547\times 10^{-4}P-7.72\times 10^{-7}P^2] \qquad (8)$$

with P in kbar. The quantity $\frac{1}{3}(C_{11}+2C_{12})$ and the directly measured bulk modulus are in reasonable agreement for gold at room temperature.

Combining Eqs. (5), (7), and (8) and values for the several constants appropriate to gold, and with r_0 assumed to have the value 6.38 F, we obtain

$$\Delta E=-0.01172(\Delta r_0/r_0)(\Delta V/V)$$
$$=(\Delta r_0/r_0)[6.501\times 10^{-6}P-0.905\times 10^{-8}P^2], \qquad (9)$$

with ΔE in eV. The solid curve shown in Fig. 3 represents a least-squares fit of Eq. (9) to the "black" points, and the value of the change of nuclear size corresponding to this is $\Delta r_0/r_0=1.50\times 10^{-4}$. We feel that we have measured the coefficient of $\Delta R^{-3}/R^{-3}$ in Eq. (7) to perhaps 15% but it is more difficult to estimate an error for $\Delta r_0/r_0$ because it depends on the model used for ΔE, Eqs. (6) and (7) and more importantly on our use of the Wigner-Seitz model to calculate values for $|\psi_P(r_0)|^2$ and its logarithmic derivative, Eq. (5). The above 15% error is sufficiently large to include all of the measured points, Fig. 3.

As was mentioned, our estimate of $|\psi_P(r_0)|^2$ may be too high in that U has been treated as though it were of purely s character. In this sense the value for $\Delta r_0/r_0$ may be near but is probably larger than the value $+1.50\times 10^{-4}$ given above. This would be in the direction to agree more closely with a value $\sim+3\times 10^{-4}$ given by Shirley *et al.*[4] A positive sign for $\Delta r_0/r_0$ is in qualitative accord with a nuclear model in which the

[22] J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).
[23] K. A. Gschneidner, Jr., in *Solid State Physics 16*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), p. 275.

first-excited state of gold is thought to be based on a vibrational state of the nuclear core.[24] Our observed $\Delta r_0/r_0$ is quite small, however, and an adequate calculation of this quantity may require the consideration of the wave functions for the individual nucleons as well as of the collective motion of the nucleus.

The result, Eq. (9) can be expressed in terms of the equivalent Doppler velocity $v(P)$. Then

$$v(P)=g(\Delta R^{-3}/R^{-3})=-g(\Delta V/V)$$
$$=g[5.547\times10^{-4}P-7.72\times10^{-7}P^2]. \quad (10)$$

The solid line in Fig. 3 corresponds to a value of g of 0.68 ± 0.1 cm/sec. This error is sufficiently large to include all of the measured points in Fig. 3.

Equation (10) gives the isomer shift in terms of the change of the average density of the gold $\Delta R^{-3}/R^{-3}=-\Delta V/V$ with compression. Equations (2), however, give $v(P)$ in terms of the change of electron density at the gold nucleus $[|\psi_P(r_0)|^2-|\psi_0(r_0)|^2]/|\psi_0(r_0)|^2$. Through Eqs. (4) and (5) we may use the Wigner-Seitz model to relate the electron-density change at the nucleus to the change in average density of gold with compression. Thus we may write

$$\frac{|\psi_P(r_0)|^2-|\psi_0(r_0)|^2}{|\psi_0(r_0)|^2}=\frac{\Delta|\psi(r_0)|^2}{|\psi(r_0)|^2}$$
$$=\frac{\Delta C(R)}{C(R)}=0.86\frac{\Delta R^{-3}}{R^{-3}}. \quad (11)$$

Combining Eqs. (10) and (11), we obtain the result

$$v(P)=g\frac{\Delta R^{-3}}{R^{-3}}=\frac{g}{0.86}\frac{|\psi_P(r_0)|^2-|\psi_0(r_0)|^2}{|\psi_0(r_0)|^2}$$
$$=G\frac{|\psi_P(r_0)|^2-|\psi_0(r_0)|^2}{|\psi_0(r_0)|^2}. \quad (12)$$

Thus the G of Eq. (2b) is given as

$$G=g/0.86=0.8\pm0.1 \text{ cm/sec} \quad (13)$$

within the Wigner-Seitz model.[14]

In the earlier paper[6] mentioned above, we obtained a value for this quantity G in the range 0.7–0.8 cm/sec. Thus the values for G obtained from the earlier alloy work and from the present high-pressure work agree both as to sign and as to magnitude within experimental error. To this extent, the earlier screening model[6] for the isomer shift in alloys, and our present high-pressure isomer-shift measurements interpreted in the Wigner-Seitz approximation are in close agreement. Because both of these models are at best approximate in character the closeness of the agreement of the two measurements of G may be fortuitous in some degree.

[24] A. De-Shalit, Phys. Letters **15** (2), 170 (1965).

The present high-pressure Mössbauer study supports a conclusion based on measurements by Shirley *et al.*[4] as well as our own,[5,6,25] namely, that for gold dissolved in Li, Be, Mg, Al, Si, Ca, Cu, Ag, Zn, Cr, V, Mn, Fe, Co, Ni, Ge, Sn, Te, Se, Y, Pd, and Pt—all of the gold alloys which have been studied so far as we are aware—$|\psi(r_0)|^2$ for Au in the alloy is greater than it is in metallic gold.

Within the above interpretation of our high-pressure measurements in terms of the Wigner-Seitz model, the present work and previous results[5,6] indicate that even though the average number of s-band electrons per atom in nickel is less than in gold,[26] in a dilute Au-Ni alloy, the charge density near the gold nucleus is $\sim70\%$ greater[6] than it is in metallic gold. Similarly for dilute Au-Pd and Au-Pt alloys, this charge density is, respectively, $\sim30\%$ and $\sim20\%$ greater than in gold metal. These results have a bearing on the nature of the screening process for gold in these metals.

It is sometimes assumed in a first approximation[27,28] that for, say, one atom of gold in palladium, the s band will not be perturbed by the impurity atom; that due to the relatively high d-band density of states, there is an appreciable spatial variation of charge density due to the impurity in the d band only. It may be expected, however, that the s band will be perturbed somewhat, although perhaps only in a small degree in comparison with the perturbation of the d band. The Matthiessen resistance which the gold introduces in the palladium is directly related to this s-band perturbation.

As was mentioned in Sec. I, in the screening model which we have previously used[6] to describe the isomer shift for, say, Au in Pd, it is assumed that the Pd conduction or s band is in fact perturbed by the Au impurity and that the isomer shift for the Au is an aspect of this perturbation. This model is in accord with the above result that $|\psi(r_0)|^2$ for Au in Pd and Pt is greater than it is for pure gold. Because this model and the present high-pressure work give within error the same value for G, Eq. (13), we suggest that the screening model for the isomer shift may be a useful approximation and may be of value in obtaining an estimate of the s-band perturbation for dilute solutions of Au in Cu, Ag, Pd, and Pt.

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[25] D. Erickson, Louis D. Roberts, and J. O. Thomson, Phys. Rev. (to be published).

[26] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 581.

[27] F. Gautier and P. Lenglart, Phys. Rev. **139**, A705 (1965).

[28] J. Friedel, Nuovo Cimento Suppl. **2**, 287 (1958).

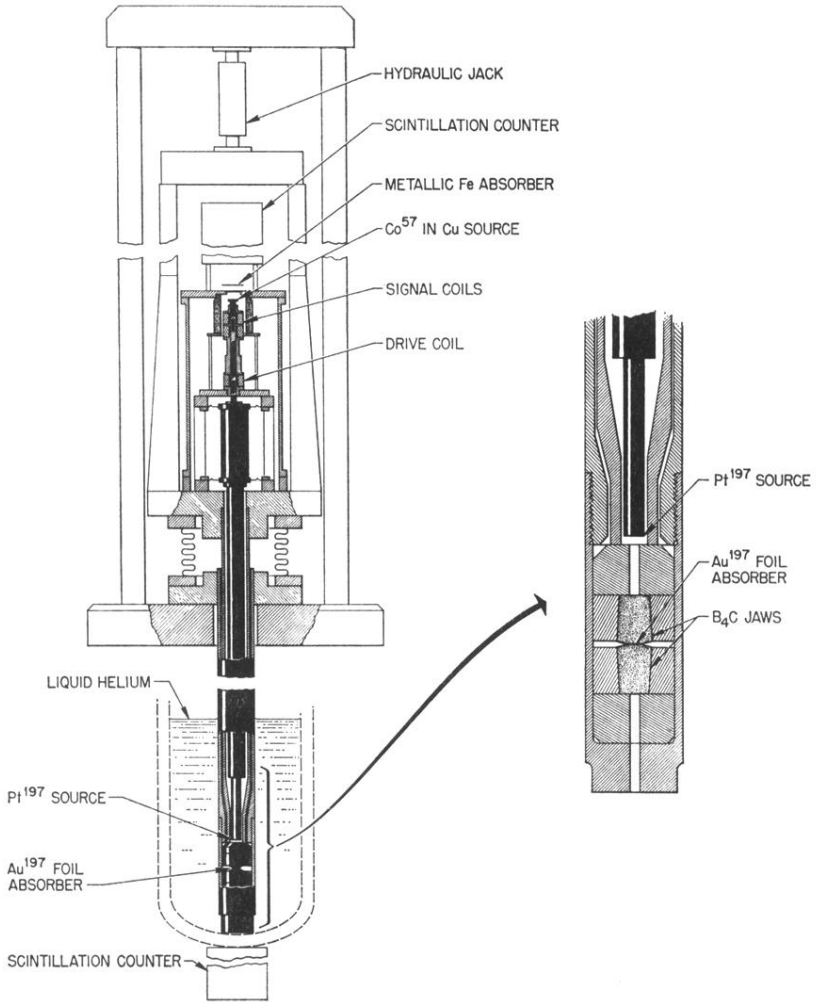

FIG. 1. Apparatus which was used for making Mössbauer-effect measurements at high pressures and at liquid-helium temperatures. A ^{197}Pt source is mounted at the lower end of the armature of the transducer and a ^{57}Co in Cu source at the upper end. This makes it possible to measure the pressure dependence of the resonance γ ray of gold relative to the 6-line hyperfine structure spectrum of the resonance γ ray of ^{57}Fe in metallic iron. The parts of the apparatus, other than the jaws, which may be under a high tensile stress were fabricated from the maraging steel Vascomax 300. Each of the jaws of the press was fabricated by forcing a 1% oversize tapered plug of B_4C into a hardened Vascomax 300 steel ring. With this arrangement, the B_4C plugs have been loaded to approximately twice the compressive strength of an unsupported B_4C cylinder without failure. The B_4C jaws were used so that a high pressure could be applied to the gold sample with a minimum γ-ray attenuation. The question of the uniformity of the pressure is discussed in the text.