Electron-electron interaction from the pressure dependence of the Mössbauer isomer shift of metallic tin

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We have measured the pressure dependence of the Mössbauer isomer shift $S(P)$ for metallic tin in some detail from 81 to 126 kbar. These results were combined with our earlier tin $S(P)$ measurements to obtain information about the isomer shift for $0 \leq P \leq 310$ kbar. The lowest pressure at which evidence for a phase transition was found was 92 kbar, in agreement with earlier work. Thus the pure single phase, Sn-I, was found to extend from 0 to 92 kbar. The transition showed a hysteresis loop which displayed structure on the side of the loop for increasing pressure. The median pressure of the loop was about 100 kbar. The pure single phase, Sn-II, was found to occur for pressures from about 108 kbar to the highest pressures at which we have made measurements. We have calculated $S(P)$ for the pure single phases, Sn-I and Sn-II, in the relativistic augmented-plane-wave model. In these calculations exchange and correlation were treated in the Kohn-Sham, in the Hedin-Lundqvist, or in the Slater model. The Kohn-Sham and the Hedin-Lundqvist models agreed with the $S(P)$ measurements from about 20 to 175 kbar. The Hedin-Lundqvist model gave perhaps the better agreement. The range of reciprocal volume over which agreement was found was about 21% of $1/V_0$. None of these models led to agreement for the entire pressure range, $0 \leq P \leq 310$ kbar.

I. INTRODUCTION

The electron-electron interaction in a solid is a function of the distance between the electrons. Thus a study of the pressure, or average electron density, dependence of some suitable solid-state property may provide a useful way to study this interaction. In several recent publications we have suggested that the study of the Mössbauer isomer shift[1] as a function of pressure, $S(P)$, for metallic tin may be suitable for this purpose.[2-7]

Within an atom, as a function of radius, the electron density increases as the distance from the nucleus decreases. Correspondingly, the electron-electron interaction, which is attractive, and which depends on the electron density, contributes qualitatively an attractive central potential to the total potential of the atom.

A number of theoretical models have been proposed to describe the electron-electron interaction. A particular model, when it describes a stronger interaction will tend, through the above effective central potential, to draw more electron density into the central region of the atom. The Mössbauer isomer shift depends on the electron density in the central region of the atom, or more precisely on the electron density $\rho(0)$ at the nucleus.[1] In this way, the Mössbauer isomer shift, in part, depends upon and thus contains information about the electron-electron interaction.

For these reasons the study of the pressure dependence of the Mössbauer isomer shift can provide a tool for the investigation of the electron-electron interaction. We have suggested that tin is the best Mössbauer element for this purpose.[2-4]

A. Earlier studies

In recent publications[2,3] we described measurements of $S(P)$ for metallic tin for the pressure range 0–310 kbar. In this work, the pressure was generated through the use of a diamond-anvil clamp,[8-10] and was measured by the ruby-fluorescence method.[8-10] The present work is a continuation of this earlier study.

For the above range of pressure, the density of the tin increases by about 30% and there is a phase transition near 92 kbar.[11] In the lower-pressure phase, Sn-I, the tin has a tetragonal structure with two atoms in the unit cell. In the high-pressure phase, Sn-II, the structure is also tetragonal, but with one atom in the unit cell.[11]

In a recent paper[2] we used our measurements of the pressure dependence of the Mössbauer isomer shift for tin, in combination with relativistic augmented-plane-wave[12] (RAPW) calculations[2,3] of the tin isomer shift, as a tool in a study of the electron-electron interaction. We showed that for tin, away from the 92-kbar phase transition, the calculated slope $[dS(P)/dP]_P$ has a dependence on the description of exchange and correlation used in the RAPW calculation. This dependence was comparable to or larger than our measurement errors. Thus a comparison between the measured and the calculated isomer shifts was able to give information about the electron-electron interaction. In this recent paper[2] we have listed references to other earlier studies of $S(P)$ for tin.

B. Tin isomer shift near the 92-kbar phase transition

In our previous measurements of $S(P)$, no Mössbauer-isomer-shift measurements were made in the

immediate vicinity of the 92-kbar phase transition. We found in this earlier study,[2,3] however, that it would have been helpful in the interpretation of the isomer-shift data, and in the study of the electron-electron interaction, to have had more detailed $S(P)$ data through the phase-transition region.

Here, we describe additional, more detailed, isomer-shift measurements for tin for the pressure range from 81 to 126 kbar.[7] This pressure range is through the phase-transition region. We wished to obtain more precise information about the pressure region over which the transition occurs, and a more accurate value for the total change of the measured isomer shift across the phase transition. In the latter part of this paper we will use this data, together with our earlier measurements of $S(P)$, in a study of the electron-electron interaction.

II. THE MÖSSBAUER ISOMER SHIFT

The Mössbauer isomer shift[1−4,7] is described by the relations

$$S(P) = (2\pi/3)(c/E_\gamma)Ze^2 \Delta \langle r^2 \rangle g \Delta\rho_P(0) \tag{1a}$$

$$= \alpha g \Delta\rho_P(0) \tag{1b}$$

$$= \alpha g [\rho_P(0) - \rho_R(0)] , \tag{1c}$$

$$\alpha = [S(P') - S(Q)]/g[\rho_{P'}(0) - \rho_Q(0)] , \tag{1d}$$

$$\alpha = [dS(P)/dP]_P / g[d\rho_P(0)/dP]_P . \tag{1e}$$

Here, c is the velocity of light, E_γ is the energy of the Mössbauer γ ray, Ze is the nuclear charge, and $\Delta \langle r^2 \rangle$ is the change of the nuclear mean-square charge radius which occurs when the resonance gamma ray is absorbed. $\rho_P(0)$ is the electron density at $r = 0$, viz., at the center of a tin nucleus at a pressure P. $\rho_P(0)$ is obtained from an RAPW calculation. $\Delta\rho_P(0)$ is the difference between the total electron density at $r = 0$ within the tin nucleus in the Mössbauer absorber at a pressure P and a selected reference electron density $\rho_R(0)$. g is the factor by which we multiply $\Delta\rho_P(0)$ to obtain the difference of the electron densities averaged over the nuclear volume. g was found to have a value[2] $g = 0.975$.

A. Constants to be determined

For the isomer shift $S(P)$ in Eqs. (1), there are two constants to be determined. These are the Mössbauer-isomer-shift calibration constant α, and a value for the selected reference electron density at the nucleus $\rho_R(0)$. We will determine these constants from the two equations, Eqs. (1c) and (1d), from two measured values for the isomer shift, $S(P')$ and $S(Q)$, and from $\rho_{P'}(0)$ and $\rho_Q(0)$. The latter two electron densities at the nucleus at the pressures P' and Q were calculated in the RAPW model. See Sec. III.

We will not expect our calculated $S(P)$ to describe the pressure dependence of the tin isomer shift in the region of pressure where the tin sample is actually changing phase. We will compare the calculated $S(P)$ with the measured $S(P)$ for pressures outside of the transition re-

gion where the tin is in a single pure phase. We will wish the calculated $S(P)$ to apply to as much of a given single-phase region as possible. Thus, in the determination of α and $\rho_R(0)$, P' will be a selected pressure just above, and Q a selected pressure just below, the tin 92-kbar phase transition.

In the following, as in our earlier paper,[2,3] we will select $Q = 90$ kbar as the lower of these pressures and P' will be selected to have a value of 108 kbar as a pressure just above the phase transition.[7] The isomer shift at P' and at Q will be obtained in Sec. VII. With values for α and $\rho_R(0)$, a relationship between $S(P)$ and $\rho_P(0)$ is specified by Eq. (1c) for all P away from the phase transition.

B. Information about the electron-electron interaction

The values for α and $\rho_R(0)$ which we obtain will depend on the theoretical model for exchange and correlation used in the RAPW calculations of the electron density at the nucleus, $\rho_P(0)$, which appear in Eqs. (1). Thus, for pressures away from the phase transition, we may use Eq. (1c) to compare the measured $S(P)$ with the $S(P)$ calculated from $\rho_P(0)$ for several different treatments of exchange and correlation. Through this comparison, which will be made in Sec. VIII, we will seek to obtain information about the electron-electron interaction in terms of its contribution to the tin isomer shift.[2,3,7]

III. RAPW CALCULATIONS OF THE ELECTRON DENSITY AT THE NUCLEUS AS A FUNCTION OF PRESSURE AND FOR SEVERAL MODELS FOR EXCHANGE AND CORRELATION

In an earlier paper[2,3] we have described, in some detail, RAPW calculations of the $\rho_P(0)$ of Eqs. (1) for metallic tin. These calculations included contributions from both valence and core electrons and have some elements of self-consistency.[2,3,13] They were made as a function of pressure for a range of pressures through the phase transition, and for the treatment of exchange and correlation in the Kohn-Sham[14] (KS), Hedin-Lundqvist[15] (HL), and Slater[16] (SL) models. The same RAPW band-structure computational programs were used for all of these calculations. We will use the results of these earlier RAPW calculations in the discussion of our $S(P)$ measurements here.

For a given crystal-structure phase, and a given model for exchange and correlation, these earlier calculations were made first as a function of the tin atomic volume.[12] The Mössbauer-isomer-shift measurements, however, were made as a function of pressure. To compare the calculated with the measured isomer shifts, we have used several experimental pressure-volume relationships, $P(V)$, to obtain the calculated $\rho_P(0)$ of Eqs. (1) as a function of pressure. For the region of pressure below the 92-kbar phase transition we used the $P(V)$ measured by Barnett et al.[11] by a high-pressure x-ray method. For the region of pressure above the phase transition we previously used the results of Walsh et al.[17] and Al'tshuler et al.[18] to obtain $P(V)$.

TABLE I. Electron density at the tin nucleus $\rho_P(0)$ calculated as a function of pressure in a RAPW model using a KS, HL, or a SL model for the electron-electron interaction. In order to obtain an electron density, add the number from column 1 to a number in the same row from columns 2-8.

	Pressure (kbar)						
	0	30	60	90	108	178	288
	Wigner-Seitz radius (a.u.)						
	3.512	3.451	3.398	3.353	3.337	3.263	3.185
Electron density at the nucleus, $\rho_P(0)$ (a.u.), Kohn-Sham							
Core							
190 434.619	0.000(5)	0.224(5)	0.443(5)	0.651(5)	0.801(5)	1.198(5)	1.664(5)
Valence							
77.86	0.00(5)	−0.53(5)	−1.24(5)	−1.60(5)	2.88(10)	2.26(10)	2.22(10)
Total							
190 512.48	0.00(5)	−0.31(5)	−0.80(5)	−0.95(5)	3.69(10)	3.46(10)	3.89(10)
Electron density at the nucleus, $\rho_P(0)$ (a.u.), Hedin-Lundqvist							
Core							
190 438.611	0.000(5)	0.223(5)	0.442(5)	0.648(5)	0.799(5)	1.199(5)	1.664(5)
Valence							
78.81	0.00(5)	−0.58(5)	−1.32(5)	−1.75(5)	2.72(10)	2.06(10)	1.97(10)
Total							
190 517.42	0.00(5)	−0.35(5)	−0.88(5)	−1.10(5)	3.52(10)	3.26(10)	3.63(10)
Electron density at the nucleus, $\rho_P(0)$ (a.u.), Slater							
Core							
191 750.511	0.000(5)	0.185(5)	0.369(5)	0.546(5)	0.688(5)	1.026(5)	1.441(5)
Valence							
86.78	0.00(5)	−0.93(5)	−1.79(5)	−2.38(5)	1.85(10)	0.84(10)	−0.28(10)
Total							
191 837.29	0.00(5)	−0.74(5)	−1.42(5)	−1.84(5)	2.54(10)	1.87(10)	1.16(10)

Recently, Olijnyk et al.[19] have described high-pressure x-ray measurements of $P(V)$ for tin for the pressure region above the phase transition. In their work, the pressure was measured by the ruby-fluorescence method which we have used in the present high-pressure Mössbauer-isomer-shift measurements.

In Table I, for convenient reference and also to avoid ambiguity, we have reproduced our earlier RAPW results for the electron density at the nucleus[2,3] but with a new pressure scale for pressures above the phase transition. For pressures below the phase transition we have again used the $P(V)$ function measured by Barnett et al.[11] For pressures above the 92-kbar phase transition we have obtained pressure values from the recent $P(V)$ results of Olijnik et al.[19] In comparison with the earlier measurements of Walsh et al.[17] and of Al'tshuler et al.,[18] the change of the pressure scale for pressures above the transition is about 10%.

A. Many-body potentials used

The many-body potentials $V_i(r)$ which we have used in the RAPW calculations of Table I are described by

$$V_i(r) = -J[(3/\pi)\rho_P(r)]^{1/3}, \qquad (2a)$$

where

$$J = \tfrac{3}{2} \quad \text{[Slater (Ref. 16)]}, \qquad (2b)$$

$$J = 1 \quad \text{[Kohn-Sham (Ref. 14)]}, \qquad (2c)$$

and

$$J = J(x) \quad \text{[Hedin-Lundqvist (Ref. 15)]}, \qquad (2d)$$

with

$$J(x) = 1 + Bx \ln(1 + (1/x)),$$

and with

$$B = 0.7734, \quad x = r_s/21, \quad r_s = \{3/[4\pi\rho_P(r)]\}^{1/3},$$

where $\rho_P(r)$ is the total electron density at r and at the pressure P.

IV. HIGH-PRESSURE MÖSSBAUER-ISOMER-SHIFT EXPERIMENTS

The experimental conditions for the present set of tin high-pressure isomer-shift measurements near the 92-kbar phase transition were much the same as those described in our earlier paper about tin isomer-shift mea-

surements for the pressure range 0–310 kbar.[2,3] Experimental details about the Mössbauer-isomer-shift and high-pressure measurements, not sketched below, may be found there.

A diamond-anvil clamp was used for the present measurements from 81 to 126 kbar. The same clamp and Mössbauer spectrometer were used here as for our earlier tin high-pressure measurements.[2,3] The metallic tin Mössbauer absorber was prepared from isotopically separated tin containing 94% [119]Sn. The absorber was mounted in a rhenium gasket[2,3] in a sample cell 0.15 mm in diameter. The diameter of the tin sample precisely matched the diameter of the cell. We used a 16:3:1 mixture of methanol, ethanol, and water as the pressure-transmitting fluid.[9] The rhenium gasket was mounted so that the Sn sample cell was carefully centered between the diamond-anvil faces. The measurements were made at ambient temperature, 294–298 K. The pressure in the sample cell was measured at the center and near the periphery of the sample volume by the ruby-fluorescence method.[8–10] To do this, a number of ruby chips about 0.025 mm in diameter were placed in the sample cell along with the tin Mössbauer absorber. Ruby fluorescence– pressure readings were usually made at three or four of these chips.

V. MEASUREMENT OF THE PRESSURE

The wavelength of the ruby $R1$ fluorescence line increases with the pressure applied to the ruby. The relationship which we have used[10] between the pressure P and the incremental increase with pressure, $\Delta\lambda(P)$ Å, of the wavelength of the $R1$ fluorescence line is given by

$$P = 3808\left(\left\{[\Delta\lambda(P)/(6942\ \text{Å})]+1\right\}^5 - 1\right)\ \text{kbar} . \quad (3)$$

For our pressure range of 81–126 kbar the three or four ruby chips almost always gave the same pressure reading to within 0.1–0.2 kbar. The measured pressure was taken to be the average of the readings for the several ruby chips.

A. Relaxation of the pressure

With our tin Mössbauer source strength of a few tenths mCi and because of the quite small size of the Mössbauer absorber, an isomer-shift measurement at a given pressure required one to two weeks of counting time. The pressure was measured each day. This measurement procedure gave some information about any pressure relaxation that might occur in the sample cell. For a pressure change of say 100 kbar, there was a relaxation of a few kbar over a period of 24 h after which the pressure reading was stable. For smaller pressure changes of say 10 kbar or less, no relaxation of the pressure was observed.[7]

VI. ISOMER-SHIFT MEASUREMENTS THROUGH THE 92-KBAR PHASE TRANSITION: A HYSTERESIS LOOP

The additional, new results of our tin isomer-shift measurements[7] through the 92-kbar transition are shown
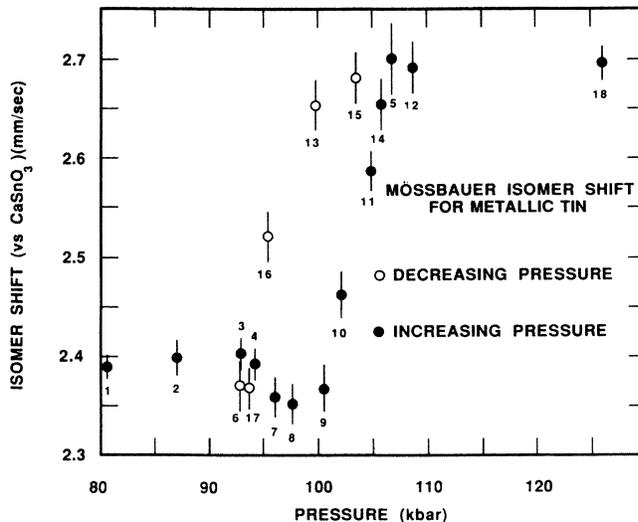

FIG. 1. Pressure dependence of the Mössbauer isomer shift $S(P)$ for tin in the vicinity of the 92-kbar phase transition.

in Fig. 1. It was found that with increasing and/or decreasing pressure the isomer-shift data in the immediate vicinity of the transition described a hysteresis loop.[7] This hysteresis phenomenon does not seem to have been observed before. The chronological order of the measurements is indicated by the numbers associated with the experimental points in this figure. When going between points on opposite sides of the hysteresis curve, say from 13 to 14, the pressure was decreased until it was well below the transition at about 70 kbar and then increased to the desired pressure at 14. Alternatively, when going from 14 to 15 the pressure was raised to around 150 kbar and then lowered to the desired value in the transition region. Points described by solid circles were obtained as a part of a sequence of measurements with increasing pressure while points described by open circles were a part of a measurement sequence with decreasing pressure.

Within the time scale of our measurements,[7] the shape of the hysteresis loop appears to be independent of time. We say this because the measurement sequences, 4 to 5 to 6, 13 to 14, and 14 to 15, each of which involved only a relatively short time, and points 7 through 12, where the measurements required some months, all fall on a smooth curve.

Since the several ruby chips gave the same pressure[7] within error, and since the pressure which was read did not appear to depend on time, we suggest that the pressure measured by the ruby chips was the same, within measurement error, as the pressure applied to the tin sample. If this should be the case, the hysteresis phenomena are a property of the tin sample, not an aspect of the pressure measurement.

A. Sharp dip in $S(P)$

The isomer shift at points 7 and 8, within the hysteresis loop, dips or falls sharply below that at points 2,

3, and 4 which are outside of the loop. This may perhaps be seen better in Fig. 3—to be discussed below—where all of our $S(P)$ measurements for tin are shown.

On the scale of the pressure effects which we are studying, the dip is fairly large and sharp. The amplitude of the dip is, for example, about one third of the decrease of $S(P)$ between 0 and 90 kbar. The width of this dip, however, is only a few kbar.[7]

B. Transition pressure

Barnett et al.[11] have given 92 kbar as the transition pressure. In our results, this is close to the pressure at which the last trace of the high-pressure phase disappeared with decreasing pressure. With increasing pressure 92 kbar is close to the pressure at which the above dip in the measured $S(P)$ begins. Phenomena related to the transition seem to begin, or to end, near 92 kbar. We also have taken 92 kbar to be the pressure which characterizes the transition.

VII. VALUES FOR THE TIN ISOMER SHIFT AT THE PRESSURES $P' = 108$ AND $Q = 90$ KBAR

In Fig. 2, we show the new data[7] of Fig. 1 along with isomer-shift measurements in this pressure region that we had made previously.[2,3] As described in the figure caption, we have fitted straight lines by least squares to
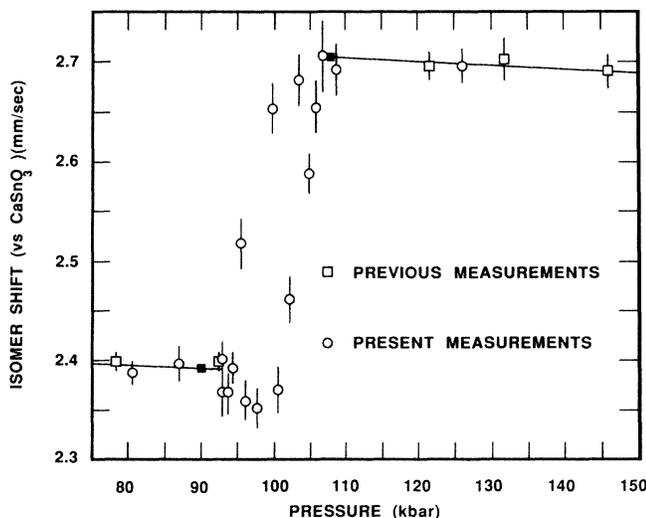

FIG. 2. Isomer-shift measurements of Fig. 1 along with tin isomer-shift measurements made previously, Refs. 2, and 3. These measurements, taken together, are used to determine the isomer shift at 90 kbar, $S(90)$, and at 108 kbar, $S(108)$. These isomer shifts are taken to be in the single-phase regions just below and just above the pressure region of the hysteresis loop. The value for $S(90) = 2.3921 \pm 0.005$ mm/sec is displayed in the figure by a small solid square. It was obtained from a least-squares line fitted to the six lowest-pressure points shown. Similarly, $S(108) = 2.7048 \pm 0.005$ mm/sec was obtained by extrapolation back from the four highest-pressure isomer-shift points. It is also shown in the figure by a small solid square.

the measured points above and below the phase transition. These lines are shown in Fig. 2. We thus obtain $S(90) = 2.3921 \pm 0.005$ mm/sec and $S(108) = 2.7048 \pm 0.005$ mm/sec with

$$S(108) - S(90) = 0.3127 \pm 0.007 \text{ mm/sec} . \qquad (4)$$

VIII. COMPARISON OF THE KS, HL, AND SL MODELS FOR EXCHANGE AND CORRELATION WITH THE HIGH-PRESSURE MÖSSBAUER MEASUREMENTS

From Table I, we obtain the result that $\rho_{P'}(0) - \rho_Q(0)$ has the values $4.64a_0^{-3}$, $4.62a_0^{-3}$, and $4.38a_0^{-3}$ where the RAPW calculations were made using the KS, HL, or SL descriptions of exchange and correlation. Here a_0 is the first Bohr radius. From Eq. (4) we have the result that $S(P') - S(Q)$ has the value 0.3127 mm/sec. With $g = 0.975$ and Eqs. (1c) and (1d), we can calculate the fitting parameters, α and $\rho_R(0)$, for each of the models, KS, HL, and SL, for exchange and correlation. For α, from Eqs. (1d) and (4), we obtain the values $0.0692a_0^3$ mm/sec, $0.0695a_0^3$ mm/sec, and $0.0732a_0^3$ mm/sec for the KS, HL, and SL interactions.

With the fitting parameters, α and $\rho_R(0)$, the calculated $S(P)$ for each model for exchange and correlation, KS, HL, and SL, will pass precisely through the experimental points at $S(Q)$ and $S(P')$ near the phase transition.

Figure 3 shows the results of all of our $S(P)$ measurements[2,3,7] for tin for $0 \le P \le 310$ kbar. In this figure, we may see how the RAPW calculations of $S(P)$, using the KS, HL, and SL interactions, compare with the measured $S(P)$ for pressures away from the phase transition.

A. Pressure ranges of agreement for the KS and HL models

It would generally be expected that the KS or HL model should lead to a better agreement of the calculated with the measured $S(P)$ than would be obtained for the SL model. For the pressure ranges from about 20–90 kbar, and from 108 to about 175 kbar, the measured $S(P)$ and the calculated $S(P)$ agree within experimental error for the KS and HL interactions. Of these two interactions, for the pressure range 20–90 kbar the HL model perhaps may give a slightly better agreement with experiment. At 20 kbar the reciprocal volume $V_0/V = 1.035$, and at 175 kbar, $V_0/V = 1.25$ for tin.[11,19] Thus, apart from the pressure region of the phase transition, the KS or the HL model leads to agreement of the calculated with the measured $S(P)$ for a range of reciprocal volume of about 21% of $1/V_0$.

Let us consider other values for P' and Q. We may, for example, calculate α for the KS and HL interactions from Eq. (1d) with any P' in the approximate range $108 \le P' \le 175$ kbar above the phase transition together with any Q in the approximate range $20 \le Q \le 90$ kbar below the phase transition. When we do this, α will be found to have a value near 0.069, close to the value found above for $P' = 108$ and $Q = 90$ kbar. Thus, α will be found to be invariant within error to the choice of P'
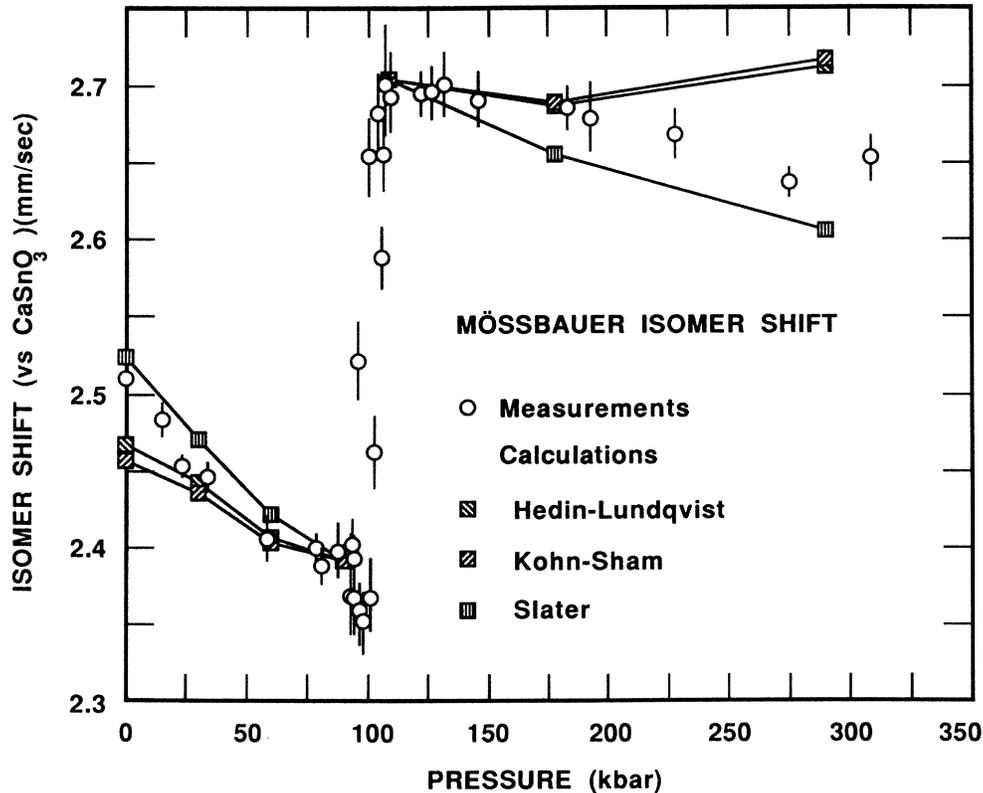
FIG. 3. Complete set of our high-pressure Mössbauer-isomer-shift measurements for tin. The pressure scale here is 5 times more dense than that of Fig. 2, and several points shown in Fig. 2, which are near 94 kbar, do not appear clearly here. This figure shows the hysteresis loop, and it also shows the dip of the measured points that occurs just within the loop and in the part of the loop for increasing pressure (see Fig. 1).

and Q in these pressure ranges.

We may also calculate α for $20 \leq P \leq 90$ and for $108 \leq P \leq 175$ kbar from Eq. (1e). Here the accuracy of the calculated α will be less than that obtained above because the accuracy of the calculation of the derivatives in Eq. (1e) is poor. Within this poorer accuracy, however, α is again found to be independent of the pressure.

B. Disagreement

For pressure in the ranges $0 \leq P \leq 20$ or $175 \leq P \leq 290$ kbar the slopes of $S(P)$ and of $\rho_P(0)$ become appreciably different. If we calculate α from Eq. (1e) for these outer pressure ranges, we will find values appreciably different from 0.069. This would seem to imply a pressure dependence for α.

C. Comments

From Eqs. (1a) and (1b), α is given by

$$\alpha = (2\pi/3)(c/E_\gamma)Ze^2\Delta\langle r^2 \rangle . \qquad (5)$$

There are no pressure-dependent quantities, at least for our range of pressures, in Eq. (5) for α. α cannot depend on the applied pressure. Thus, the apparent dependence of α on P, above, must be due to errors in the RAPW model[2,3,12] or in the models for exchange and correla-

tion.[14-16] If the models were completely correct, α would be a constant, independent of P.

The accuracy of a calculation of $S(P)$ depends in particular on the correctness of the potential and of the band-structure wave function in the interatomic region.[2,13] In comparison with our RAPW–muffin-tin calculations, we believe that an improved treatment of the potential in the interatomic region will provide a useful basis for a further study of the KS, HL, SL, or other models for the electron-electron interaction, through the Mössbauer-isomer-shift method used above.

IX. SUMMARY

New measurements have been made of the Mössbauer isomer shift of metallic tin from 81 to 126 kbar. These measurements, which are shown in Fig. 1, provide more detailed information about the behavior of the isomer shift as a function of pressure through the phase transition at 92 kbar. In Fig. 3, the isomer-shift-measurements of Fig. 1 are combined with our earlier measurements to show results for $S(P)$ for $0 \leq P \leq 310$ kbar.

In the approximate pressure range $92 \leq P \leq 108$ kbar, the isomer shift as a function of pressure was found to describe a hysteresis loop with a median pressure of about 100 kbar. With increasing pressure, within the

loop, and just above 92 kbar, there is a sharp, narrow dip in the isomer shift as a function of P. This may be a precursor of the transition with increasing P. The change of isomer shift across the transition was found to have the value $S(108) - S(90) = 0.3127 \pm 0.007$ mm/sec. As in the measurements of Barnett et al., the lowest pressure at which evidence for a phase transition was found was approximately 92 kbar. We also have taken 92 kbar to be the pressure which characterizes the transition.

For the range of pressure we have studied, Fig. 3, the Sn-I phase was found to occur for approximately $0 \leq P \leq 92$ kbar, and the Sn-II phase was found for approximately $108 \leq P \leq 310$ kbar. We have suggested that the calculated $S(P)$ for Sn should depend on the description of the electron-electron interaction used in the calculation. We have made RAPW calculations of $S(P)$ for the Kohn-Sham, the Hedin-Lundqvist, and the Slater models for this interaction. We found that the KS and HL models provided agreement with experiment, within experimental error, for the pure phase regions, $20 \leq P \leq 90$ and $108 \leq P \leq 175$ kbar. The HL model may give slightly better agreement with experiment than the KS model for $20 \leq P \leq 90$ kbar. The range of pressure, from 20 to 175 kbar, corresponds to a range of tin metallic density of about 21% of $1/V_0$.

In a continuation of the above study of the electron-electron interaction, one would seek a band-structure model and a description of the electron-electron interaction for which the above density range of agreement would be extended. In an empirical way, it may be possible to extend the range of agreement somewhat with the present RAPW band-structure model if calculations were made with a J of Eqs. (2b) or (2c) in the vicinity of 1.2 to 1.3. A value for J in this range would be larger than that which would be indicated by the x-α model.[20] We have not as yet sought to explore this possibility.

The RAPW−muffin-tin treatment used here[2,3,12] provides an approximate treatment of the potential and of the wave function in the interatomic region of the tin. We believe that, in the study of the electron-electron interaction by the high-pressure−isomer-shift method, it will be of value to improve the potential and the band-structure wave function for this interatomic region.

Our experimental data have sufficient accuracy to discriminate between the SL and the KS or HL interactions. It would be helpful to obtain Mössbauer data of sufficient accuracy to discriminate between the KS and HL models. This should be possible.

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