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Systematics of the pressure dependence of the electron density at the nucleus for the elements Ag through Te: Pressure dependence of the Mössbauer isomer shift for Sn and Sb†

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Experimental Mössbauer isomer shift studies have shown that when β-Sn is compressed, the charge density $\rho(0)$ at the nucleus decreases, viz., $\partial \ln\rho(0)/\partial \ln V > 0$. This fact suggested a study of the systematics of $\partial \ln\rho(0)/\partial \ln V$ for the Ag row of the Periodic Table. We have calculated $\partial \ln\rho(0)/\partial \ln V$ for the elements Ag through Te in a Hartree-Dirac-Wigner-Seitz approximation. Exchange is treated through an exchange potential. These calculations indicate that both valence- and core-electron contributions play a role in determining $\partial \ln\rho(0)/\partial \ln V$. *In the Wigner-Seitz model,* a positive sign for $\partial \ln\rho(0)/\partial \ln V$ for β-Sn (i.e., the sign which agrees with experimental high-pressure Mössbauer isomer shift studies) is obtained only if the exchange multiplier lies in the range $1.3 \leq \zeta \leq 1.5$, where $\zeta = 1.5$ corresponds to full Slater exchange. These Wigner-Seitz model calculations indicate a negative sign for $\partial \ln\rho(0)/\partial \ln V$ for Ag, Cd, and In, and a positive sign for this derivative for Sb, and Te. The sign for Sn depends on ζ, as indicated.

I. INTRODUCTION

Some years ago the pressure dependence of the Mössbauer isomer shift was investigated for β-Sn, an element with a half filled s-p shell. In these studies by Möller and Mössbauer[1] and by Panyushkin and Voronov,[2] β-Sn was found to behave in an exceptional way in that the total contact electron density $\rho(0) = |\psi(0)|^2$ *decreases* with increasing pressure, viz, $\partial \ln\rho(0)/\partial \ln V > 0$ where V is the atomic volume. In contrast, for gold,[3-5] an element with one valence s-p electron (and also for Fe, Eu, and Ta),[6] Mössbauer studies showed the more usual behavior, i.e., $\partial \ln\rho(0)/\partial \ln V < 0$. For the latter metals, $\rho(0)$ *increases* with pressure. Theoretical treatments for iron[7] and gold[3,4] both show that the magnitude of this increase for these metals can be explained primarily through an approximately inverse volume dependence of the valence-band contact electron density. This behavior is qualitatively similar to that of a free-electron gas, where $\rho(0)$ would have a simple $1/V$ dependence. Obviously, the volume dependence of $\rho(0)$ in β-Sn is qualitatively the opposite of that of a free-electron gas.

Rather than viewing the perhaps unusual behavior of β-Sn as an isolated case, it may be of value to examine the systematics of $\partial \ln\rho(0)/\partial \ln V$ for the rows of the Periodic Table. It is of particular interest to do this for the row beginning with silver because the elements Sn-Cs are all suitable for Mössbauer studies.

In the following, we will write

$$\gamma = \frac{\partial \ln\rho(0)}{\partial \ln V}\bigg|_{V_0}, \tag{1}$$

where γ is taken at the zero pressure atomic volume V_0 of the element.

We will use the relativistic Wigner-Seitz (WS) model[4] to obtain an approximate description of the systematics of $\rho(0)$ and of γ for the series of elements Ag through Te. Results will be given in somewhat greater detail for Sn and Sb than for the other elements in this series. In the WS model, compression is simulated[4] simply by a decrease of the WS cell volume, which is the same as the atomic volume V.

Our use of the WS model for this discussion of systematics derives from an earlier treatment of the pressure dependence of $\rho(0)$ and of the Mössbauer isomer shift for Au in the WS model.[3,4] The value of the nuclear size change $\delta\langle r^2\rangle$ obtained for ^{197}Au in this earlier work is in agreement with more recent studies.[5,6]

In this earlier work,[4] we found that when a WS Au atom was compressed from a very low density $V^{-1} \sim 0$ to the normal density of gold and on to higher densities, the calculated $\rho(0)$ went through a minimum. For gold this minimum occurred at a very low density compared to that of metallic gold, and the possible existence of such a minimum did not seem to be accessible to experimental investigation. Such minima have also been noted previously in calculations of $\rho(0)$ vs V^{-1} for hydrogen in the WS model[4] and for the 4s state of iron[7] at the bottom of the band in a modified tight-binding model.

In our present work, we find that a minimum occurs in the calculated WS $\rho(0)$ vs V^{-1} for all of the elements Ag through Te. These calculations indicate that there are two noteworthy factors in the systematics of γ with increasing atomic number from $Z = 47$ to $Z = 52$. The minimum in the calculated curves for $\rho(0)$ vs V^{-1} moves toward higher density and the zero pressure density V_0^{-1} of the elements decreases with increasing Z. These points will be explored in Sec. II.

In order to be able to see the trends mentioned above and to be described below, we make calculations of $\rho(0)$ over a wide range of reciprocal atomic volume V^{-1} or, that is, of the density of an element. In this context the use of the WS model to study trends may be of value. (Of course the free-atom model which is frequently used to obtain estimates of $\rho(0)$ does not offer a choice of atomic volume.) For very small values of V^{-1} compared to the normal value V_0^{-1} of an element, the concept of crystal structure may not be meaningful; for very high values of V^{-1} this structure may not be known. Although band-structure effects are omitted in the WS model, over the range of V^{-1} considered this model should give a useful estimate of the wave functions of the core states and of the valence-band states near the bottom of the band. To this extent the WS model may give a qualitatively correct picture of the true volume dependence of $\rho(0)$ and may thus be useful in a preliminary study of the systematics of γ vs atomic number. Our calculations have been made on this premise. See also Sec. V.

A. Wigner-Seitz model

In the WS calculation of $\rho(0)$ we have used a computer program[4] which treats the atomic many-body problem in the self-consistent-field approximation. The Dirac equation is used to describe the motion of the individual electrons. The self-consistent potential used is of the Hartree type, and exchange may be included approximately in the form of an exchange potential. The self-consistent calculation of course includes the core states.

In the WS model, the atoms in the metal are treated in spherical symmetry. Each electron state can then be characterized by the principal quantum number n, by the orbital angular momentum quantum number l of the large component of the wave function, and by the total angular momentum quantum number j. We may write the total electron contact density as

$$\rho(0)=\sum_{nlj}^{Z} \rho_{nlj}(0)\,, \tag{2}$$

where Z is the atomic number of the atoms making up the metal, and $\rho_{nlj}(0)$ is the contribution to the charge density at the nucleus due to the nlj shell. Only $ns_{1/2}$ and $np_{1/2}$ electrons will contribute to $\rho(0)$.

As Crawford and Schawlow[8] and Mallow *et al.*[8] have observed, a valence s electron will have a significant amplitude in the inner region of an atom and will contribute to the screening of the core states. Valence p and d states will of course contribute to core screening also. When an atom is compressed, the change, $\delta|\psi_c(0)|^2/|\psi_c(0)|^2$, for the core states due to the above screening may be very small compared to unity. Nevertheless, $\delta|\psi_c(0)|^2$ may be significant compared to $\delta|\psi_V(0)|^2$ for the valence states. In the present work the contribution of the core states to γ is found to be of some significance. As will be seen, for the Ag row of the Periodic Table, this contribution is due predominantly to the $4s_{1/2}$ electrons and is of particular interest for Sn. See Sec. III.

B. Numerical treatment

In the present application we make particular use of four features of the program[4]: (i) We may impose a boundary condition on each electron wave function of the atom such that the large component will have zero slope at the WS radius, R_{WS}. $R_{\text{WS}}=(3V/4\pi)^{1/3}$, where $V=V(P)$ is the volume per atom at an applied pressure P. The wave functions are normalized within V. (ii) The program[4] uses an exchange potential $U_{\text{ex}}(r)$ which, in atomic units, is

$$U_{\text{ex}}(r)=-\zeta[3\rho(r)/\pi]^{1/3}\,. \tag{3}$$

$\rho(r)$ is the total electron density at r, and ζ is a constant which may be varied in the program. $\zeta=\frac{3}{2}$ corresponds to full Slater exchange, $\zeta=1$ corresponds to Kohn-Sham exchange, and $\zeta=0$ corresponds to the omission of exchange from the calculation, in which case we have used the Hartree approximation.[4,9] We give calculations of $\rho(0)$ for $\zeta=0$, 1, and $\frac{3}{2}$. The qualitative results which we have obtained are fairly insensitive to the value of ζ except in the case of Sn. γ is quite sensitive to ζ for Sn, and, in the WS model, it is found to change sign as ζ is varied. This will be discussed in Sec. III. (iii) Another feature of the program which we have utilized is its ability to converge for electronic configurations other than that of the ground state. We have obtained solutions for several Sn and Sb valence-state configurations, and, to this degree, we have investigated the effects of crystal structure on $\rho(0)$ and γ. (iv) In all calculations we have used a nucleus of finite extent with a charge distribution of the Fermi shape.[4] The nuclear radius and surface diffuseness parameters used ranged from 5.1404 and 0.5666 fm, respectively, for Ag to 5.4268 and 0.5666 fm, respectively, for Te. In our numerical treatment of the WS model,[4] the innermost grid point was at about $5\times10^{-6}a_0$ which is much less than the nuclear radius. Our values of $\rho(0)$ are the calculated values at the center of the nucleus.

The calculation was iterated until the total potential and each subshell potential at each of about 250 grid points were self-consistent to one part in 10^6. Also each subshell eigenvalue was brought to a self-consistency of at least one part in 10^6.

The procedure by which numerical values of, for example, $\partial\rho_{nlj}(0)/\partial \ln V$ were obtained is as follows: the wave-function program[4] was run for a particular exchange multiplier and electronic configuration with $R_{WS}=0.99R_{WS}(V_0)$ and then with $R_{WS}=1.01R_{WS}(V_0)$, where $R_{WS}(V_0)$ is the zero-pressure WS radius. From the $\rho_{nlj}(0)$ thus calculated, the $\partial\rho_{nlj}(0)/\partial \ln V \equiv \Delta\rho_{nlj}(0)/\Delta \ln V$ were evaluated at the zero-pressure WS volume V_0.

II. SYSTEMATIC BEHAVIOR OF ρ (0) vs V^{-1} FOR THE ELEMENTS Ag THROUGH Te

In Fig. 1 we show graphs of the Wigner-Seitz $[\rho(0)-\rho_0(0)]/\rho_0(0)$ vs V^{-1} for the elements Ag through Te. Here $\rho_0(0)$ is the total contact density of an element, Eq. (2), at the zero-pressure atomic, or WS volume V_0. Table I gives R_{WS}, V_0^{-1}, the valence configurations used, and the calculated WS $\rho_0(0)$ for these elements. The curves shown in Fig. 1 were calculated with Kohn-Sham exchange, viz., with the exchange multiplier $\zeta=1$ in Eq. (3).

As may be seen in Fig. 1, there is a minimum in the total $\rho(0)$ vs V^{-1} for each element. With increasing atomic number Z this minimum moves to higher values of V^{-1}. Conversely, with increasing Z, the normal reciprocal volume or density V_0^{-1} moves to lower values of V^{-1}.

We find that the calculated WS $\rho(0)$ vs V^{-1} for Ag is quite similar to that for gold[4] in that this calculated minimum is at a very low density compared to the normal density V_0^{-1} of the metal. As in the case of Au, the minimum for Ag is inaccessible to direct experimental study. However, with increasing Z, the position of the minimum and V_0^{-1} move toward each other. For β-Sn the minimum is very nearly at the normal metallic density V_0^{-1}, and for Sb and Te the minimun occurs at a density V^{-1} greater than V_0^{-1}. Thus the minimum phenomenon becomes accessible to study in the sense that for each element a small piece of the $\rho(0)$ vs V^{-1} curve is in an observable region of V^{-1}.

In Fig. 1 we have shown results for the total contact density $\rho(0)$. This total contact density may be separated into two parts $\rho(0)=\rho_c(0)+\rho_v(0)$. Here, $\rho_c(0)$ is the contact density due to core $s_{1/2}$ and $p_{1/2}$ electrons. We define the core $s_{1/2}$ and $p_{1/2}$ states as those which *do not* have a significant wave-function amplitude at R_{WS}, i.e., $\psi_c(R_{WS})$ is near zero. $\rho_v(0)$ is the contact density due to valence-band electrons, i.e., to those s and p electrons which *do* have a significant amplitude $\psi_v(R_{WS})$ at R_{WS}. This will enable us to speak of a core contribution and a valence contribution to $\partial\rho(0)/\partial \ln V$. For the elements Ag through Te the core contribution is then due to electrons through the $n=4$ shell, and the valence-band contribution is due to $5s_{1/2}$ and $5p_{1/2}$ electrons.

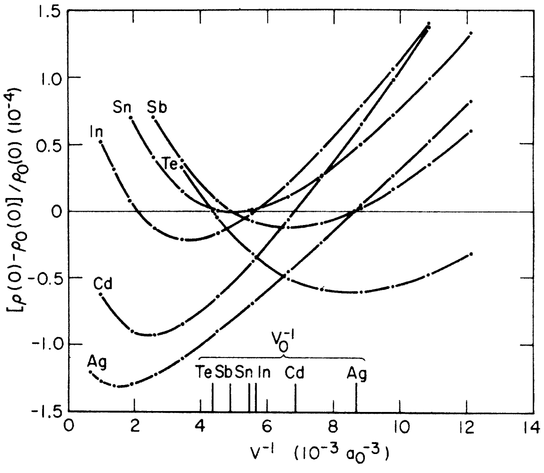

FIG. 1. Electron density at the origin vs atomic density V^{-1}. Curves are shown for the row of elements: Ag, Cd, In, Sn, Sb, and Te. All of the curves were calculated in a relativistic self-consistent-field approximation using Wigner-Seitz boundary conditions and Kohn-Sham exchange. These calculated electron densities are shown in terms of the fraction $[\rho(0)-\rho_0(0)]/\rho_0(0)$, where $\rho(0)$ is the total charge density at the origin as a function of the atomic density V^{-1} and $\rho_0(0)$ is this charge density at the zero-pressure atomic density V_0^{-1}. The valence configurations used and the values for V_0^{-1} and $\rho_0(0)$ are given in Table I. Each curve in the figure shows a minimum. The minimum for Ag is at an atomic density V^{-1} much less than the normal density V_0^{-1} for Ag. For Sn, the minimum is at a value of V^{-1} close to the normal density V_0^{-1} for Sn; and for Sb and Te, the minima occur at atomic densities greater than the normal densities. Thus, for this family of curves, the sign of the slope evaluated at V_0^{-1} changes with increasing atomic number. This result is given in more detail in Table I and in Fig. 2.

We find then for all of the elements Ag through Te and for the entire range of V^{-1} covered in these calculations $\partial\rho_c(0)/\partial \ln V<0$. The core electrons do not contribute in a direct way to the minima shown in Fig. 1. Rather for all of these elements, $\rho_c(0)$ increases with V^{-1} for the range of V^{-1} studied here.

The minimum phenomenon in the WS calculations is an aspect of the screened $5s_{1/2}$ and $5p_{1/2}$

TABLE I. Calculated volume dependence of electron contact density for the elements Ag through Te. Self-consistent relativistic wave functions were calculated in a Wigner-Seitz approximation with Kohn-Sham exchange ($\zeta = 1$) for the specified valence configurations. The zero-pressure Wigner-Seitz radii (R_{WS}) used, corresponding atomic densities (V_0^{-1}), and calculated core [$\rho_{\text{core}}(0)$], valence [$\rho_{5s1/2}(0)$, $\rho_{5p1/2}(0)$], and total [$\rho(0)$] contact charge densities, along with their derivatives, are all given in atomic units. The total charge densities are given for other V^{-1} in Fig. 1, and the derivatives $\gamma = \partial \ln \rho(0)/\partial \ln V$ are plotted in Fig. 2.

$\zeta = 1$ Configuration Pd($4d^{10}$) core plus	Ag $5s^1_{1/2}$	Cd $5s^2_{1/2}$	In $5s^2_{1/2}5p^1_{1/2}$	Sn $5s^2_{1/2}5p^2_{1/2}$	Sb $5s^2_{1/2}5p^2_{1/2}5p^1_{3/2}$	Te $5s^2_{1/2}5p^2_{1/2}5p^2_{3/2}$
$R_{\text{WS}}(V_0)$	3.017 44	3.264 10	3.478 23	3.519 75	3.652 18	3.796 80
V_0^{-1} (10^{-3})	8.689 18	6.864 43	5.673 09	5.474 69	4.900 48	4.361 56
$\rho_{\text{core}}(0)$	145 290.62	159 118.09	174 174.49	190 434.62	208 210.38	227 314.95
$\partial\rho_{\text{core}}(0)/\partial \ln V$	−9.55	−8.74	−6.11	−4.02	−2.24	−2.35
$\rho_{5s1/2}(0)$	23.26	42.25	44.84	55.24	73.70	102.40
$\partial\rho_{5s1/2}(0)/\partial \ln V$	−19.69	−24.74	−11.92	−0.07	19.54	34.58
$\rho_{5p1/2}(0)$			0.44	1.03	1.27	1.71
$\partial\rho_{5p1/2}(0)/\partial \ln V$			−0.34	−0.55	−0.27	0.06
$\rho(0)$	145 313.88	159 160.34	174 219.77	190 490.89	208 285.35	227 419.05
$\partial\rho(0)/\partial \ln V$	−29.24	−33.47	−18.37	−4.64	17.04	32.29
$\gamma = \partial \ln \rho(0)/\partial \ln V$ (10^{-4})	−2.012	−2.103	−1.054	−0.244	0.818	1.420

electrons for this series of elements. There is a minimum in both the WS $\rho_{5s1/2}(0)$ and the $\rho_{5p1/2}(0)$ (for those elements having $5p_{1/2}$ electrons) vs V^{-1} for all of the elements, Ag through Te [e.g., $\rho_{5s1/2}(0)$ for Sn in Fig. 3]. But since $\rho_{5p1/2}(0) \ll \rho_{5s1/2}(0)$, the minimum phenomena are predominantly due to screened $5s_{1/2}$ electrons. In the case of Sn, however, $\partial\rho_{5p1/2}(0)/\partial \ln V$ may be of some significance. See Sec. III.

In Fig. 2 we give a graph of γ vs atomic number for $\zeta = 1$ and $\zeta = \frac{3}{2}$. γ is less than zero for Ag, Cd, and In, is approximately zero for Sn, and is greater than zero for Sb and Te. γ is sensitive both to atomic number and to the value of the exchange multiplier ζ.

From Fig. 2 we see that, for $\zeta = 1$ or $\zeta = \frac{3}{2}$, Sn, which has a half-filled valence shell, plays a pivotal role in that $\gamma \sim 0$. For $\zeta = 1$, $\gamma \sim -2.4 \times 10^{-5}$. This may be compared to the change of γ, say, from In to Sn or from Sn to Sb, $\Delta\gamma/\Delta Z \sim 10 \times 10^{-5}$. Thus, charging or screening effects, relatively small in comparison with a change of atomic number, may be able to change the sign of γ for Sn. Mössbauer isomer shift measurements give $\gamma < 0$ for Sn in Mg_2Sn, but $\gamma > 0$ for β-Sn.[1,2] Alloying and crystal structure thus do have an effect[1] on the experimental or true sign of γ. The sign of γ for Sn in Mg_2Sn or for β-Sn is related to the screening of the $5s_{1/2}$ electrons in these materials, as Möller and Mössbauer observed.[1] It also seems reasonable to suggest, on the basis of the above remarks, that the change of the sign of γ between β-Sn and Mg_2Sn is related to the fact that Sn is pivotal, i.e., that as a function of atomic number γ is close to zero for Sn.

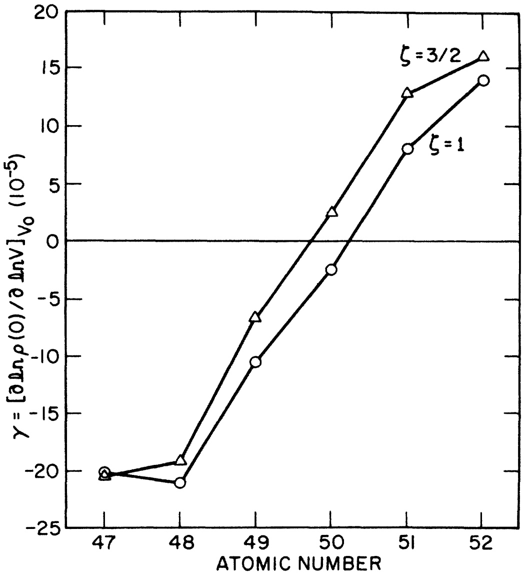

FIG. 2. Volume dependence of contact charge density vs atomic number. The volume dependence of the electron density $\rho(0)$ at the origin (nucleus) is expressed as $\gamma = \partial \ln \rho(0)/\partial \ln V$ and is evaluated at the zero-pressure atomic volume V_0. The points are calculated in a relativistic self-consistent-field approximation using Wigner-Seitz boundary conditions. Two curves are shown, one using full Slater exchange ($\zeta = 1.5$) and one using Kohn-Sham exchange ($\zeta = 1.0$). The value of γ for Ag [and also for gold (Ref. 4)] is nearly independent of the exchange multiplier. The other elements have $\gamma(\zeta = 1.5) > \gamma(\zeta = 1.0)$. γ crosses zero in the vicinity of Sn. Thus effects smaller than a change of Z, such as solid state or chemical effects, may change the sign of γ for Sn. For the elements of this series with $Z < 50$, γ is negative, and for the elements with $Z > 50$, γ is positive. γ is near zero for the half filled valence shell of Sn.

In (Sec. III) we investigate the sensitivity of the sign of γ to the value of ζ and to atomic configuration for Sn and Sb, and we calculate the corresponding pressure dependence of the Mössbauer isomer shifts for these elements. A comparison with experiment is made for Sn.

III. PRESSURE DEPENDENCE OF THE MÖSSBAUER ISOMER SHIFTS FOR Sn AND Sb

In a customary notation,[6] the volume derivative of the Mössbauer isomer shift S may be given by

$$\frac{\partial S}{\partial \ln V} = \alpha\gamma\rho(0) = \alpha \sum_{nlj}^{Z} \frac{\partial \rho_{nlj}(0)}{\partial \ln V}, \tag{4}$$

where the proportionality constant α depends only on nuclear parameters of the Mössbauer nucleus. For S in mm/sec and $\rho(0)$ in atomic units, $\alpha(^{119}\mathrm{Sn}) = 0.093 \pm 0.010 a_0^3$ mm/sec for tin[10] and $\alpha(^{121}\mathrm{Sb}) = -0.28 \pm 0.09 a_0^3$ mm/sec for antimony.[11] $\alpha(^{119}\mathrm{Sn})$ and $\alpha(^{121}\mathrm{Sb})$ are of opposite sign.

A. Tin

In Fig. 3 we show the calculated effect of compression on that part of the contact density for Sn due only to the two $5s_{1/2}$ valence electrons in the $5s_{1/2}^2 5p_{1/2}^2$ configuration which is assumed here. Two curves are shown, one calculated with full Slater exchange, $\zeta = \frac{3}{2}$, and one without exchange[9], $\zeta = 0$. We see the following: (a) The magnitude of $\rho_{5s1/2}(0)$ increases as ζ is changed from 0 to $\frac{3}{2}$. (b) The minimum in $\rho_{5s1/2}(0)$ vs V^{-1} occurs in each curve near the density V_0^{-1} corresponding to β-Sn. (c) The position of the minimum is affected by the value of ζ. (d) For the curve with $\zeta = \frac{3}{2}$ and at the normal density of β-Sn, $\rho_{5s1/2}(0)$ decreases when the density of the solid is increased. Thus for $\zeta = \frac{3}{2}$, $\partial\rho_{5s1/2}(0)/\partial \ln V > 0$. It thus has the same sign as the total γ [Eq. (4)], which is measured[1,2] for β-Sn by the Mössbauer method, i.e., $\partial S/\partial \ln V > 0$.

In Table II we give calculated values for contact densities and their volume dependences for β-Sn. The calculations were made for $V = V_0(\beta\text{-Sn})$, for three valence configurations, both with and without exchange. For a $5s_{1/2}^2 5p_{1/2}^2$ valence configuration, for example, $\partial\rho_{5s1/2}(0)/\partial \ln V$ is negative[9] for $\zeta = 0$. It is approximately zero at $\zeta = 1$ (Kohn-Sham exchange), and it is positive at $\zeta = \frac{3}{2}$ (full Slater exchange). $\partial\rho_c(0)/\partial \ln V$ is negative with a value of about -3 to $-4a_0^{-3}$ for all of the valence configurations studied and for all values for the exchange parameter in the range $0 \leqslant \zeta \leqslant \frac{3}{2}$. Because of this negative contribution from the core electrons, ζ must be greater than ~1.3 for the total γ [Eq. (1)] to be greater than zero in the WS model.

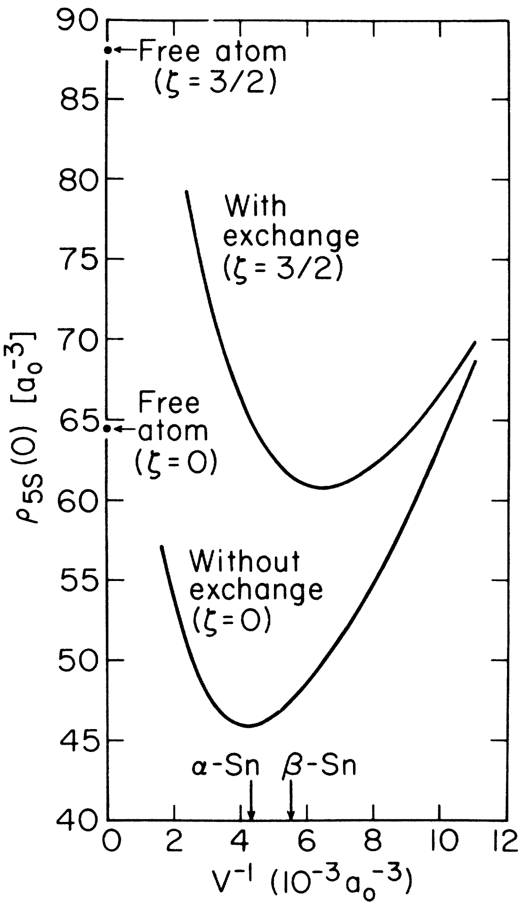

FIG. 3. Calculated $5s_{1/2}$ charge density $\rho_{5s1/2}(0)$ at the nucleus for two $5s_{1/2}$ electrons in ^{119}Sn vs metallic density. The metallic density, expressed as reciprocal atomic volume, covers a range which includes the density of β-Sn, as indicated. $\rho_{5s1/2}(0)$ is also shown for the free atom. Two curves are shown. The upper curve is for the relativistic Hartree-Slater atom ($\zeta = \frac{3}{2}$) with Wigner-Seitz boundary conditions (Ref. 4). [The free atom has its usual boundary conditions, and the Slater-Latter approximation is used (Ref. 4).] The lower curve is for the relativistic Hartree-Wigner-Seitz atom ($\zeta = 0$). Both curves exhibit a minimum in the region of metallic density of β-Sn. The valence configuration used is $5s_{1/2}^2 5p_{1/2}^2$. At the density of β-Sn, $\partial\rho_{5s1/2}(0)/\partial \ln V$ is found to be positive for $\zeta = \frac{3}{2}$ in agreement with experiment.

Figure 4 shows the rather delicate balance found in the WS model between the volume dependences of the core, the $5s_{1/2}$ and the $5p_{1/2}$ contact densities over the range of volume where β-Sn has been studied experimentally under pressure. Note that even the small change in the $5p_{1/2}$ contact density is a perceptible fraction of the change in $\rho(0)$ with $\Delta V/V$ because γ is near zero (Fig. 2).

In Fig. 4 we also show the experimental result obtained by Möller and Mössbauer[1] and by Panyushkin and Voronov.[2] The experimental

TABLE II. Calculated volume dependence of electron contact density for β-Sn. Self-consistent relativistic wave functions were calculated in a Wigner-Seitz approximation with full Slater exchange ($\zeta=\frac{3}{2}$), Kohn-Sham exchange ($\zeta=1$), and in the Hartree approximation[9] ($\zeta=0$). Results are given for three valence configurations. The core [$\rho_{\text{core}}(0)$], valence [$\rho_v(0)=\rho_{5s1/2}(0)+\rho_{5p1/2}(0)$], and total [$\rho(0)$] contact charge densities and their derivatives, all shown in atomic units, are given for atoms at a zero-pressure Wigner-Seitz radius of $3.5120a_0$.

Configuration Pd($4d^{10}$) core plus	$5s^2_{1/2}5p^2_{1/2}$			$5s^1_{1/2}5p^2_{1/2}5p^1_{3/2}$		$5s^2_{1/2}5p^2_{3/2}$	
ζ	0	1	$\frac{3}{2}$	0	$\frac{3}{2}$	0	$\frac{3}{2}$
$\rho_{\text{core}}(0)$	190 603.42	190 434.65	191 750.54	190 603.48	191 750.73	190 603.38	191 750.62
$\partial\rho_{\text{core}}(0)/\partial\ln V$	−3.77	−4.04	−3.39	−3.24	−2.87	−3.66	−3.28
$\rho_{5s1/2}(0)$	47.44	55.24	61.53	24.34	31.34	47.75	61.80
$\partial\rho_{5s1/2}(0)/\partial\ln V$	−11.43	−0.38	8.45	−4.68	5.59	−11.06	9.05
$\rho_{5p1/2}(0)$	0.98	1.03	1.11	1.00	1.13		
$\partial\rho_{5p1/2}(0)/\partial\ln V$	−0.78	−0.56	−0.43	−0.75	−0.39		
$\rho_v(0)$	48.42	56.28	62.64	25.34	32.47	47.75	61.80
$\partial\rho_v(0)/\partial\ln V$	−12.21	−0.93	8.03	−5.43	5.21	−11.06	9.05
$\rho(0)$	190 651.84	190 490.93	191 813.18	190 628.82	191 783.20	190 651.13	191 812.42
$\partial\rho(0)/\partial\ln V$	−15.97	−4.97	4.63	−8.67	2.33	−14.72	5.77

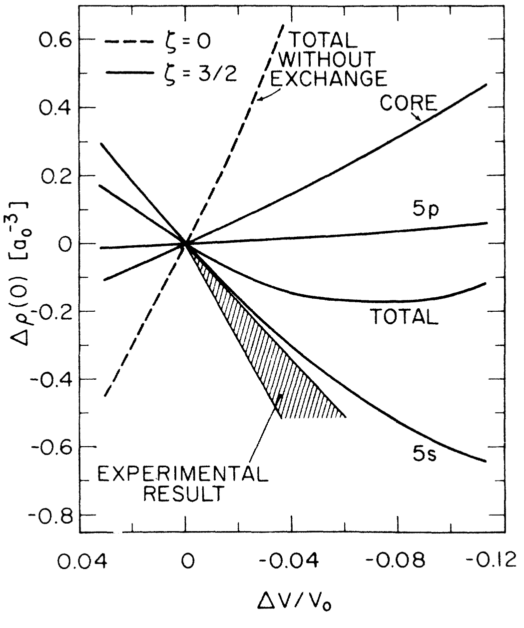

FIG. 4. Relativistic electron contact densities at the nucleus in ^{119}Sn vs metallic density. Both coordinates are expanded about the values for β-Sn at zero pressure. Curves are shown for the total charge density at the nucleus both with Slater exchange ($\zeta=\frac{3}{2}$, solid curve) and without exchange ($\zeta=0$, dashed curve). The valence configuration used is $5s^2_{1/2}5p^2_{1/2}$. For Slater exchange, the core, $5s_{1/2}$, and $5p_{1/2}$ contributions to the total show a partial cancellation of effects. The experimental values (Refs. 1 and 2) are also shown.

isomer shift data are given in the literature[1,2] as a function of pressure in graphical form. We have converted pressure to volume using the available compressibility data[12] for β-Sn and have made a straight-line fit to the six available experimental data points of S vs V. This yielded $\partial S/\partial\ln V=+1.1$ mm/sec. We then calculated $\partial\rho(0)/\partial\ln V$ from Eq. (4) using the calibration constant given above ($\alpha=+0.093a_0^3$ mm/sec). This yielded a measured $\partial\rho(0)/\partial\ln V=+12a_0^{-3}$ which is the measured slope shown in Fig. 4. We have estimated the uncertainty in this experimental slope to be about $\pm3a_0^{-3}$ due to uncertainties in α and in $\partial S/\partial\ln V$. This uncertainty is indicated in Fig. 4 by the crosshatched region.

Within the WS model when full Slater exchange ($\zeta=\frac{3}{2}$) is included, we obtain $\partial\rho(0)/\partial\ln V=+2.2$ to $+5.7a_0^{-3}$ depending on configuration, while experiment[1,2] yields $+12\pm3a_0^{-3}$. Thus with $\zeta=\frac{3}{2}$, the WS model calculation agrees with experiment as to sign but the quantitative agreement is poor.

As we have noted, in order to obtain $\gamma>0$ for tin, in the WS model, the exchange multiplier ζ must be greater than about 1.3. A smaller value for ζ closer to 1.0 may perhaps be more realistic physically. The WS model is an approximate treatment, and the larger value of $\zeta>1.3$ required here may be due to this approximate nature of the model. These WS calculations do indicate, however, that $\partial\rho(0)/\partial\ln V$ for Sn is quite sensitive

TABLE III. Calculated volume dependence of electron contact density for Sb. Self-consistent relativistic wave functions were calculated in a Wigner-Seitz approximation with full Slater exchange ($\zeta = \frac{3}{2}$) and in the Hartree approximation[9] ($\zeta = 0$). Results are given for three valence configurations. The core [$\rho_{\text{core}}(0)$], valence [$\rho_v(0) = \rho_{5s1/2}(0) + \rho_{5p1/2}(0)$], and total [$\rho(0)$] contact charge densities and their derivatives, all shown in atomic units, are given for atoms at a zero-pressure Wigner-Seitz radius of $3.651 a_0$.

Configuration Pd($4d^{10}$) core plus	$5s^2_{1/2}5p^2_{1/2}5p^1_{3/2}$		$5s^1_{1/2}5p^2_{1/2}5p^2_{3/2}$		$5s^2_{1/2}5p^1_{1/2}5p^2_{3/2}$	
ζ	0	$\frac{3}{2}$	0	$\frac{3}{2}$	0	$\frac{3}{2}$
$\rho_{\text{core}}(0)$	208 380.64	209 632.10	208 381.00	209 632.60	208 380.71	209 632.19
$\partial\rho_{\text{core}}(0)/\partial \ln V$	−1.65	−2.49	−1.10	−1.98	−1.35	−2.44
$\rho_{5s1/2}(0)$	61.14	84.13	31.83	43.36	61.22	84.46
$\partial\rho_{5s1/2}(0)/\partial \ln V$	7.65	29.55	6.04	17.02	8.80	30.10
$\rho_{5p1/2}(0)$	1.12	1.42	1.16	1.47	0.57	0.72
$\partial\rho_{5p1/2}(0)/\partial \ln V$	−0.53	−0.08	−0.47	0.01	−0.26	−0.04
$\rho_v(0)$	62.26	85.55	32.98	44.83	61.79	85.18
$\partial\rho_v(0)/\partial \ln V$	7.12	29.47	5.57	17.03	8.54	30.07
$\rho(0)$	208 442.90	209 717.65	208 413.98	209 677.42	208 442.50	209 717.37
$\partial\rho(0)/\partial \ln V$	5.47	26.97	4.47	15.05	7.19	27.63

to the treatment of exchange and correlation effects.

B. Antimony

Detailed WS calculations analogous to those for Sn have been made for Sb. Some results are listed in Table III for three valence configurations, and for[9] $\zeta = 0$ and $\zeta = \frac{3}{2}$. For Sb, $\partial\rho(0)/\partial \ln V$ is positive for all of these configurations and for the complete range of ζ values. Core electron effects are slightly smaller than those found for Sn. These calculations indicate that, like in tin, the charge density at the Sb nucleus will *decrease* when pressure is applied to Sb metal.

Based on the results given in Table III we may make an estimate of the volume dependence of the ^{121}Sb isomer shift in Sb. Using Eq. (4) and the calibration constant given earlier ($\alpha = -0.28 \pm 0.09 a_0^3$ mm/sec) we find $\partial S/\partial \ln V$ to lie in the range from −3 to −8 mm/sec.

IV. DISCUSSION OF THE MINIMUM IN $\rho(0)$ vs V^{-1}

The essential result of this paper is related to a minimum in $\rho(0)$ vs V^{-1}. In the case of hydrogen where the atom has only one electron, the occurrence of the above minimum in $\rho(0)$ as a function of V^{-1} may be viewed as an aspect of the description of metallic hydrogen in terms of the WS boundary condition.[4] For elements with a higher atomic number where there are many electrons per atom, both screening effects and the above effect of the WS boundary condition may contribute to the volume dependence of $\rho(0)$. We may see some aspects of this screening by an examination of the wave functions, Fig. 5, for example.

In Fig. 5, $5s_{1/2}$ and $5p_{1/2}$ electron densities are

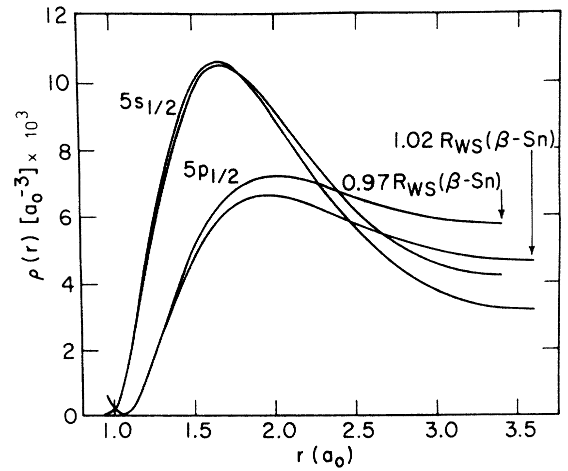

FIG. 5. The effect of compression on the valence electrons in β-Sn. The radial charge densities are shown for a $5s_{1/2}$ and a $5p_{1/2}$ electron for Wigner-Seitz radii (R_{ws}) of $3.41 a_0$ and $3.58 a_0$. The valence configuration used is $5s^2_{1/2}5p^2_{1/2}$. The compressed functions are not simply renormalized versions of the lower-pressure functions but have the positions of their outer maxima shifted. Upon compression, both $\rho_{5s1/2}(r)$ and $\rho_{5p1/2}(r)$ increase for $r \sim R_{ws}$. The increase in $\rho_{5p1/2}(r)$ extends inward to a smaller radius than does the increase in $\rho_{5s1/2}(r)$. Also note that since $\rho_{5p1/2}(R_{ws}) > \rho_{5s1/2}(R_{ws})$, more $5p_{1/2}$ charge must be displaced by compression.

shown for Sn for $\zeta = \frac{3}{2}$ and for two atomic volumes. These volumes are in the region of V^{-1} in Fig. 3, where $\rho_{5s1/2}(0)$ decreases as the atomic density V^{-1} is increased. Upon compression, both $\rho_{5s1/2}(r)$ and $\rho_{5p1/2}(r)$ increase for $r \sim R_{WS}$, but the increase in $\rho_{5p1/2}(r)$ extends inward to a smaller radius than does the increase in $\rho_{5s1/2}(r)$. Thus there is a tendency toward an enhanced shielding of the $5s_{1/2}$ electron and a corresponding tendency for $\rho_{5s1/2}(0)$ to decrease as the atom is compressed. If the Sn atom is compressed enough, however, the direct increase in $\rho_{5s1/2}(0)$ due to renormalization of the $5s_{1/2}$ wave function dominates both the effect of shielding by the $5p_{1/2}$ electrons and the effect of the WS boundary condition. Here $\rho_{5s1/2}(0)$ will increase as V^{-1} is increased. As may be seen in Table II, $5p_{3/2}$ electrons have a screening effect similar to that of $5p_{1/2}$ electrons.

V. SUMMARY

The systematics of the pressure dependence of the electron density at the nucleus have been investigated in an approximate way through the use of the WS model and results are given in some detail for the elements Ag through Te. It is found that for these elements, as a general trend γ, Eq. (1), increases with both atomic number and with the exchange multiplier ζ, Eq. (3). In the vicinity of Sn, γ passes through zero (see Fig. 2). γ is found to be predominantly due to the $5s_{1/2}$ electrons, and to the screening of these $5s_{1/2}$ electrons by other electrons in the valence shell.[1] Contributions to γ due to the core and $5p_{1/2}$ electrons should not be neglected. For tin *in the WS model* with $\zeta > \sim 1.3$ our calculated $\gamma > 0$ is in qualitative agreement with experiment. For Sb and Te, the model gives $\gamma > 0$ independent of ζ, a behavior like that found experimentally for β-Sn.

We have made preliminary Mössbauer measurements[13] of $\partial\rho(0)/\partial \ln V$ for Sb. We find that for Sb, $\rho(0)$ decreases when the metal is compressed. This result is in accord with the predictions of the above WS model and is similar to the behavior found experimentally for Sn.[1,2]

It is suggested that it may be of value to measure γ by the Mössbauer method for Te, I, Xe, and Cs. Te and I have crystal structures which are molecular rather than metallic, and Xe is a Van der Waals solid. Thus, for Te-Xe, the WS model may give but a very poor value for γ. We have calculated γ for these elements and also for Cs in the WS model, but for the above reason we do not give detailed results here for the elements beyond Te. These results may be of interest, however, for they suggest that with increasing atomic number γ will pass through a maximum positive value near Te and then decrease to pass through zero near Xe. γ will again have a negative value at Cs.

We note that in the WS model, $\gamma \sim 0$ for both Sn and Xe, which in our WS calculations were taken to have a half filled and a full s-p shell.

The sensitivity of γ to ζ, particularly for Sn, suggests that the further investigation of this derivative may be of value in the theoretical study of exchange and correlation effects in solids.

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