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Isomer Shifts and Electronic Structure of Pd-Sb Alloys

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Sb^{121} isomer shifts are presented for α-phase Pd-Sb alloys and for the compounds PdSb and $PdSb_2$. The results are compared with similar data for Pd-Sn and Pd-Au, and it is shown that they are compatible with a model in which the solute atoms are almost perfectly screened by conduction electrons.

INTRODUCTION

Of all transition metal alloys, those based on Pd are among the most attractive for the study of electronic structure. Pd has a nearly full *d* band with a paramagnetic ground state, and its band structure has recently been elucidated to a remarkable extent.[1,2] When polyvalent solutes are dissolved in Pd, the number of holes in the host *d* band is rapidly reduced, and susceptibility data indicate that the rate at which the *d* band fills is roughly proportional to the solute valency.[3,4] This behavior has frequently led to the suggestion that there is a charge transfer from the solute atoms to fill the empty *d* states on neighboring solvent sites. However, if taken literally, this suggestion is contrary to Friedel's theory of dilute alloys, which assumes that each solute atom is almost perfectly screened by conduction electrons within its own atomic volume.[5] Friedel's theory is itself open to discussion, because it is uncertain to what extent the electrons in the Pd *d* band should be considered as "conduction electrons" in the present context, and the mechanism by which the solute atoms perturb the *d* band is far from clear. Some information on the electronic structure of these alloys can be obtained from the isomer shifts in the Mössbauer spectra of the solute nuclei: These shifts arise from the change in the charge radius of a nucleus when it emits its γ ray, and they vary linearly with the electron density at the nuclear position.[5a]

The present measurements were made on Pd-Sb alloys, and our results will be compared with existing data on the Pd-Sn [4,6] and Pd-Au [7] systems. Pratt *et al.*[8] have recently studied the phase diagram of Pd-Sb, and they list the unit cell dimensions for the α-phase alloys and for the two compounds PdSb and $PdSb_2$. They find that the solubility limit of the α phase is at 17 at.%, so our own measurements were made on alloys containing up to 15 at.% Sb and on the two compounds mentioned. According to the simple rigid-band model, the density of states in α-phase Pd-Sb alloys should be the same as that of Pd-Ag alloys containing 5 times their concentration of Ag. This prediction is largely confirmed by measurements of low-temperature susceptibility[3] and specific heat,[9] although the apparent valency of Sb in Pd seems to fall at the higher concentrations, being about 4 for Pd-10% Sb. Similarly, room-temperature susceptibility data on Pd-Sn alloys give an apparent valency for Sn which is close to the expected value of 4 at low concentrations, but falls to about 3 at the phase boundary.[4] Thus, the empirical correlation between the solute valency and the rate at which the *d* band fills is clearly significant, but should not be regarded as exact.

EXPERIMENTS AND RESULTS

The specimens were derived from the same source as those used in the structural analysis mentioned above,[8] and were kindly loaned to us by Dr. J. B. Darby. After arc-melting in a helium-argon atmosphere, the ingots were homogenized for a week at 100 °C in argon and water-quenched. The α-phase alloys were rolled into foils 2 mil thick and cut into 3-cm-diam disks, which were strain relieved *in vacuo* for 1 h at 500 °C. The compounds were much too brittle to be rolled into foils, so they were each ground to powder and were strain-relieved for $\frac{1}{2}$ h at 500 °C in a pure argon atmosphere. Subsequent x-ray powder photographs confirmed the structure of both compounds. It was found that a single disk made a suitable Mössbauer absorber in the case of the solid solutions, while for the compounds each absorber consisted of a weighed amount of powder encased in a Lucite disc, the density of natural Sb being about 3 mg/cm^2. Mössbauer spectra were obtained using a standard transmission geometry and a $CaSnO_3 \times (Sb^{121})$ source, both source and absorber being at 80 °K. The 37.2-keV γ rays were detected as a 9-keV escape peak in a xenon proportional counter. Reference 10 can be consulted for further experimental details.

Each spectrum consisted of a single absorption

TABLE I. Compositions in at.%: Mössbauer data in mm/sec. $e^2q\ Q/4$ is the quadrupole splitting parameter. Specimen and source ($CaSnO_3$ Sb) are both at 80 °K. S_I is the isomer shift (a velocity of approach is positive). LW is the linewidth (full width at half-maximum).

Specimen	8-line analysis			1-line analysis	
	$e^2qQ/4$	S_I	LW	S_I	LW
Pd-2.6% Sb	0.82	− 7.04	2.30	− 7.04	2.51
Pd-5.2% Sb	0.90	− 7.07	2.32	− 7.08	2.58
Pd-7.9% Sb	0.86	− 7.10	2.48	− 7.11	2.71
Pd-103% Sb	0.93	− 7.13	2.39	− 7.14	2.67
Pd-12.9% Sb	0.84	− 7.25	2.50	− 7.25	2.71
Pd-15.0% Sb	1.15	− 7.32	2.98	− 7.30	3.34
PdSb	1.12	− 9.66	2.77	− 9.65	3.11
$PdSb_2$	1.07	−10.17	2.81	−10.18	3.12

maximum. This line is somewhat broadened over the theoretical minimum of 2.1 mm/sec, and this broadening appears to increase with increasing antimony concentration. For the compounds PdSb and $PdSb_2$, unresolved quadrupole splittings probably explain most of the broadening since the Sb atoms are located at noncubic sites.[11] For the random alloys, the linewidth probably arises partly from a spread of isomer shifts over the various solute sites, and partly from a similar spread of electric field gradients. (The lines showed no structure similar to that found in Pd-Sn alloys by Snediker.[6]) Least-squares analyses were performed on the data in two alternative ways, using the techniques described elsewhere.[10] First, each spectrum was fitted to a pattern of eight Lorentzian lines, assuming the same charge density and electric field gradient at every site and equal widths for all lines. Second, the spectra were fitted to a single Lorentzian line. Intuitively, one would expect the first procedure to be more appropriate for the compounds, and the second for the random solutions. The results of both analyses are shown in Table I.

Even for the compounds, the estimated quadrupole splitting is too small to introduce a noticeable asymmetry in the line shape, and little significance can be attached to the values obtained for the quadrupole interaction. On the other hand, both analyses give almost identical values for the isomer shifts, which are thus determined to a fair degree of accuracy. These shifts are relative to the $CaSnO_3$(Sb) source, and should be compared with the values −14.4 mm/sec for the trivalent ionic compound SbF_3 and +3.8 mm/sec for the pentavalent compound $KSbF_6$.[12] (See the left side of Fig. 1.) Crudely, when Sb is dissolved in Pd the electron density at the solute nucleus is intermediate between the values found for penta- and trivalent antimony, and is similar to those found for other metallic systems. The density increases with increasing Sb concentration.

DISCUSSION

These Mössbauer results for the Pd-Sb alloys are very similar to previous results for Pd-Sn,[4,6] as can be seen by comparing the left sides of Figs. 1 and 2. This similarity extends the conclusions of Ruby *et al.*,[12] who found that the isomer shifts for corresponding Sn and Sb chemical compounds could be closely correlated. Sn compounds have been studied more extensively than those of Sb, and the isomer shift has been shown to depend to a large extent on the state of oxidation of the Sn atoms, and on the degree of ionicity in their bonding orbitals.[13] Harris and Cordey-Hayes[4] have tentatively suggested that the isomer shifts in Pd-Sn can be interpreted in a similar way, in terms of a charge transfer from the solute to the solvent cells: Clearly, their model can also be applied to Pd-Sb.

However, as these authors point out, one must be cautious in applying concepts which are successful for insulating compounds to the problem of a metallic alloy, in which electrostatic charges are subject to powerful screening by conduction

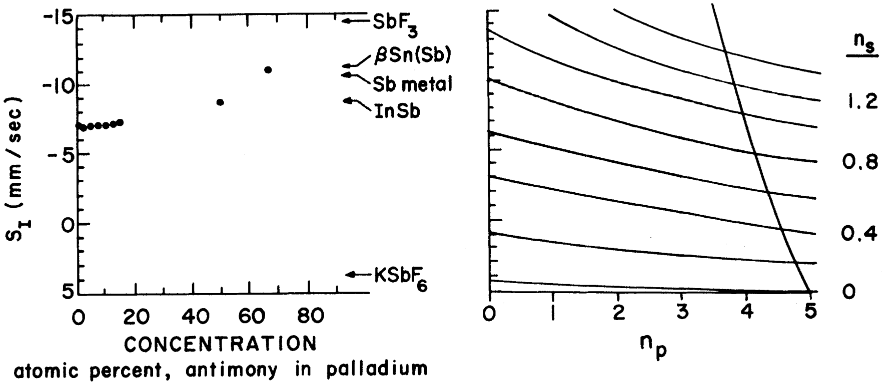

FIG. 1. Isomer shifts in Pd-Sb alloys, relative to a ($CaSnO_3$)Sb source. The information on the right-hand side of the figure is derived from Ref. 12, where the values are quoted relative to InSb: This has an isomer shift of −8.6 mm/sec with respect to the present source.

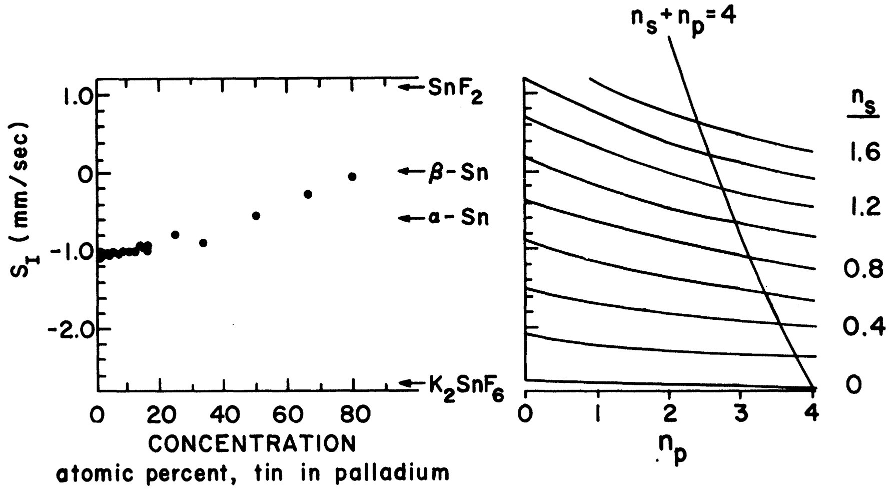

FIG. 2. Isomer shifts in Pd-Sn alloys, relative to βSn. The data for the α-phase alloys are taken from Ref. 6, those for the compounds from Ref. 4, and the information on the right-hand side of the figure from Ref. 12.

electrons. For example, in the case of β-brass, Mott has emphasized that each Zn atom cannot denote 0.5 electron to a neighboring Cu atom, because the ensuing Madelung energy would prevent an order-disorder transition at any temperature below the melting point.[14] Mott estimated that the total charge transfer in β-brass is about 0.07 electrons, which is compatible with the small latent heat measured at the transition temperature. It should be noted that his model does not assume that any valence electrons are localized on Zn sites: All the valence electrons have wave functions which extend throughout the crystal, but on the average their amplitudes are higher on a Zn site than on a Cu site. Pd alloys are of course more complicated than CuZn, but systems such as Pd-Cu do show order-disorder transitions,[15] and PdCd is ordered but can be disordered by cold work.[8] This strongly suggests that to a first approximation each atomic cell in these alloys is electrically neutral, in agreement with Friedel's general theory.[5] Thus the filling of the Pd *d* band should arise not from a charge transfer from solute to solvent, but from a conversion of *s* electrons into *d* electrons within the Pd cells. It seems likely that this picture is roughly correct for α-phase Pd-Sn and Pd-Sb, although the situation for the intermetallic compounds is more doubtful, and more information on their conductivity and order-disorder behavior would be of great interest.[16]

We now consider the electronic structure of Pd-Au alloys, whose Mössbauer spectra have been studied experimentally and theoretically by Roberts *et al.*[7] The susceptibility of Pd-Au alloys follows a simple rigid-band behavior, with an apparent valency of unity[17]: Unlike the case of Pd-Sn and Pd-Sb, the electron density at the Au^{197} nucleus is higher in the alloys than in the pure solvent metal. Roberts *et al.* present a detailed calculation of the screening of the Au atoms by *s* electrons, and they are able to correlate the isomer shifts and the residual resistivities for alloys in which Au is dissolved dilutely in a variety of hosts: The systems they consider explicitly are Cu-Au, Ag-Au, Ni-Au, Pd-Au, and Pt-Au. They have also confirmed the value they used for the factor relating the isomer shift to the electron density, by making a theoretical and experimental study of the Au^{197} Mössbauer effect at high pressures.[18] Montgomery *et al.*[19] have extended their model in a qualitative way, in an attempt to consider the effect of the Au atoms in perturbing both the *s* and *d* bands of a Pd matrix.

Harris and Cordey-Hayes suggest that Pd-Au follows the screening model, while Pd-Sn follows the charge transfer model: We shall now argue that the isomer shifts for all the Pd alloys are at least compatible with the screening model. The situation in Pd-Sn and Pd-Sb is complicated by the fact that the isomer shifts depend critically on the relative *sp* character of the screening electrons. This is demonstrated on the graphs on the right-hand sides of Figs. 1 and 2, which have been replotted from Ref. 12. They display the results of Hartree-Fock self-consistent field calculations for free Sn and Sb atoms, related to isomer-shift measurements in the manner discussed in that paper. The calculated isomer shift can be expressed in the form

$$S_I = f(n_s, n_p), \qquad (1)$$

where n_s and n_p are the numbers of *s* and *p* electrons in the outermost shell. It will be noted that the electron density at the nucleus increases with n_s, but it decreases slowly with n_p, because *p* electrons tend to screen the nucleus from electrons of *s* character. It is clearly a poor approximation to apply these calculations to solute atoms in a Pd alloy, and they will be used merely to suggest qualitative trends. The assumption that the solute cell is neutral requires the equation

$$n_s + n_p = Z , \tag{2}$$

where Z equals 4 for Sn and 5 for Sb. Combining Eqs. (1) and (2), we can estimate n_s and n_p in the following way. The locus of Eq. (2) is shown as a curve on the graphs, and the intersection of an experimental isomer shift with this curve gives the values of n_s and n_p in any particular case. Thus, for βSn, n_s is about 1.2, while for dilute Pd-Sn alloys, n_s is about 0.9, increasing slightly with concentration. Very similar results seem to apply to Pd-Sb. The true situation is of course complicated by the "compression" of the solute atoms by the Pd matrix, and it does not seem possible at the moment to put these arguments onto a quantitative basis.

In addition to their measurements on Pd-Sn, Harris and Cordey-Hayes[4] present some very interesting measurements on ternary Pd-Ag-Sn alloys, each containing 2 at.% of Sn. They plot the Sn^{119} isomer shift as a function of concentration of Ag, and they find a pronounced knee at the composition at which the filling of the Pd *d* band is complete: This is contrasted with the situation in Pd-Au, where the isomer shift varies smoothly across the entire alloy field. (In Pd-Sn and Pd-Sb the phase boundary intervenes just as the *d* band is filled, so that one cannot investigate this aspect of their spectra.) Such a knee is to be expected on the charge transfer model, but it is also to be expected on the screening model. Although the detailed mechanism by which the solute atoms perturb the Pd *d* band is unclear, the basic screening problem is different when *d* holes are present or absent on the Pd sites.[20] Hence the Pd-Au results are very puzzling, because on either model one expects to see a knee at the critical composition: Its absence is not evidence for the screening model, and the previous discussion of this point by Montgomery *et al.*[19] is mistaken. As Roberts *et al.*[7] point out, there may be some structure in the Pd-Au data which is on too fine a scale to be observed.

In conclusion, we suggest that none of the experimental results on Pd alloys positively require the use of the charge transfer model, and the general weight of evidence is against it. Our interpretations are greatly hampered by the fact that the isomer shift measures the electron density only at the nuclear position: Much more satisfactory conclusions could be drawn if we had "charge-density maps" analogous to the spin-density maps which can be obtained by neutron diffraction, and which have proved so valuable in the understanding of magnetic impurities in Pd.[21] Further progress seems to depend on the development of more exact theories such as those of Beeby[22] and Gomes and Campbell,[23] so that better use can be made of the limited experimental evidence.

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[1] L. R. Windmiller and J. B. Ketterson, Bull. Am. Phys. Soc. 12, 286 (1967); 12, 543 (1967).

[2] O. K. Andersen and A. R. Mackintosh, Solid State Commun. 6, 285 (1968).

[3] D. J. Lam and K. M. Myles, J. Phys. Soc. Japan 21, 1503 (1966).

[4] I. R. Harris and M. Cordey-Hayes, J. Less-Common Metals 16, 223 (1968).

[5] J. Friedel, Advan. Phys. 3, 446 (1954).

[5a] S. L. Ruby and G. K. Shenoy, Phys. Rev. 186, 326 (1969).

[6] D. K. Snediker, *Mössbauer Methodology* 2, edited by I. Gruverman (Plenum, New York, 1966), p. 161.

[7] L. D. Roberts, R. L. Becker, F. E. Obenshain, and J. O. Thomson, Phys. Rev. 137, A895 (1965).

[8] J. N. Pratt, K. M. Myles, J. B. Darby, Jr., and M. H. Mueller, J. Less-Common Metals 14, 427 (1968).

[9] C. T. Wei (private communication).

[10] S. L. Ruby, G. M. Kalvius, R. E. Snyder, and G. B. Beard, Phys. Rev. 148, 176 (1966).

[11] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1964), Vol. 1, p. 124.

[12] S. L. Ruby, G. M. Klavius, G. B. Beard, and R. E. Snyder, Phys. Rev. 159, 239 (1967).

[13] M. Cordey-Hayes, J. Inorg. Nucl. Chem. 26, 915 (1964).

[14] N. F. Mott, Proc. Phys. Soc. (London) 49, 258 (1937).

[15] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), p. 612.

[16] Ch. J. Raub, W. H. Zachariasen, T. H. Geballe, and B. T. Matthias, J. Phys. Chem. Solids 24, 1093 (1963).

[17] E. Vogt, Ann. Physik 14, 1 (1932).

[18] L. D. Roberts, D. O. Patterson, J. O. Thomson,

and R. P. Levey, Phys. Rev. 179, 656 (1969).

[19] H. Montgomery, G. P. Pells, and E. M. Wray, Proc. Roy. Soc. (London) A301, 261 (1967).

[20] We are grateful to Dr. J. L. Beeby for clarification on this point.

[21] G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) 89, 119 (1966).

[22] J. L. Beeby, Proc. Roy. Soc. (London) A302, 113 (1967).

[23] A. A. Gomes and I. A. Campbell, J. Phys. C 1, 253 (1968).

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Lattice-Distortion Screening Effects in the Residual Resistivity of Dilute Zinc Alloys*

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New residual-resistivity data are presented for all solutes which show an appreciable solubility in zinc (Cu, Ag, Au, Cd, Hg, Al). In contrast with some previous work for zinc, the residual resistivity per atomic percent impurity is found to be a well-defined experimental quantity. The results are discussed within the framework of Blatt's lattice-distortion model for impurity resistivity, and clear evidence is obtained for significant lattice-distortion screening effects. Some systematic departures from the model predictions are correlated with solute position in the Periodic Table.

INTRODUCTION

The model for residual resistivity due to Blatt[1] was shown by him to be very successful in accounting for regularities in the wealth of available data for monovalent alloy systems. Being a free-electron model it was not clear at that time (1957) whether the treatment could be reliably extended to the polyvalent solvents, for which there were, in any case, considerably fewer experimental data. However, it has since become clear that the Fermi surfaces of some polyvalent metals are, in fact, closer to the free-electron sphere than those of the noble metals. Zinc is particularly free-electron-like in this respect,[2] and we have obtained new experimental data for dilute zinc alloys. The main purpose of this paper is to investigate how well Blatt's model can account for them.

The chief success of Blatt's model was its ability to give a convincing explanation of the "period effect" in the residual resistivity of a series of noble metal alloys. Linde's empirical rule for $\Delta\rho$, the residual resistivity per atomic percent solute,[3] tells us that

$$\Delta\rho = a + b(\Delta Z)^2 \quad , \qquad (1)$$

where ΔZ is the valence difference between solvent Z_0 and solute Z, while a and b are constants characterized both by the solvent and by the row of the Periodic Table to which the solutes belong. An early model of Mott[4] was able to obtain the $(\Delta Z)^2$ dependence of $\Delta\rho$ by assuming for the solute atoms a Thomas-Fermi-screened Coulomb potential arising from an excess positive charge of ΔZ. Mott's value for b, however, was very much larger than observed.

On the other hand, the resistivity model of Friedel,[5] which screens the excess charge ΔZ by modifying a free-electron charge density self-consistently around each solute atom, turns out to be insensitive to the details of the solute potential. Any simple choice of potential gives a reasonable value for b. However, the value obtained is the same for every row of the Periodic Table in a given solvent, whereas the experimental data on both Cu and Ag alloys show a lower value of b for Ag row solutes than for the Cu row. Blatt was able to modify the Friedel model to account for this "period effect" by assuming that the effective excess charge on a solute atom which the electrons must screen depends on the volume occupied by a solute ion relative to a host ion. Solutes in the Ag period occupy a larger volume in any noble-metal host lattice than do corresponding Cu row solutes and this leads to a reduction in the effective charge which must be screened. This in turn reduces the electron scattering and gives a smaller value of $\Delta\rho$, as observed.

Subsequent to the appearance of Blatt's work, several authors have claimed some independent support for his "size-effect" model. In addition to some later work of Blatt and Frankhouse[6] on