tive potential is reduced and γ_G will decrease. This behavior seems to be characteristic of all metals. Thus to the extent that such force models are realistic for more complicated polyatomic solids, one may expect a similar type of behavior in their γ_G. However in the latter materials a quantitative estimate of the decrease is difficult.

There are two practical limitations to the use of these two-parameter fits for extrapolating low-pressure data on more complicated solids. The first is the frequent appearance of high-pressure phase transitions in polyatomic solids such as minerals which will limit the range of densities of a single solid phase by an unknown amount. The second is the necessity of accurately measuring the two parameters at low pressure. Unfortunately, ultrasonic measurements of B_T' do not always agree among themselves or with shock-wave data. There remains, therefore, a strong need to improve the accuracy of ultrasonic measurements of B_T' in order to obtain reliable extrapolations of solid-compression data.

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Impurity Scattering in Polyvalent Metals

John H. Tripp
Department of Physics and Institute of Materials Science,
University of Connecticut, Storrs, Connecticut 06268

and

David E. Farrell
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

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The simplest successful approximation scheme for the calculation of scattering due to nonmagnetic impurities in metals, due to Blatt, has been applied to the cases of impurities in the polyvalent hosts Be, Mg, Zn, Cd, Al, In, Sn, and Pb, extending our previous work which was restricted to zinc. The results of this extended study are compared with available residual-resistivity data and, in the case of Cd, with some new experimental data. A new well-marked regularity has emerged from this extended study. If Z and Z_0 denote the Periodic Table column numbers of impurity and host, respectively, it is found that for $Z < Z_0$ the model works very well, while for $Z > Z_0$ very little agreement with experiment is obtained. An interpretation of this behavior is proposed which offers a physical understanding of the *a priori* unexpected validity of the simple model for impurity scattering in metals.

INTRODUCTION

In a previous publication[1] it was shown how the original Blatt model[2] of impurity scattering in monovalent noble-metal alloys could be extended to provide an interpretation of the residual resistivity of impurities in the divalent metal zinc. Because of metallurgical difficulties encountered in previous work[3,4] on zinc alloys, the experimental portion of Ref. 1 was restricted to impurities which displayed a ~ 1-at.% solubility. However, it was subsequently brought to our attention[5] that very reliable data also existed[6] for both Sn and In as impurities in zinc, even though the maximum solubility of these solutes is certainly very much less than 1 at.%. The present work was begun when calculation showed that, for these solutes, the Blatt model failed completely, despite the success encountered in Ref. 1 for the solutes Cu, Ag, Au, Cd, Hg, and Al. The distinction between the two groups of solutes was so marked that it seemed worthwhile to extend the investigation in order to determine whether a similar situation existed for systems based on other solvents. This has indeed been found to be the case and the main purpose of the present paper is to suggest that the distinction provides a useful insight into the *a priori* unexpected validity of simple models of impurity scattering.

CALCULATION

The model and method of calculation are set out rather completely in Ref. 1 and will not be reproduced in detail here, the procedure used for each solvent being the same as that employed for zinc. However, it is necessary to outline the physical basis of the model in order to explain the significance of the further result of this study.

In the Friedel picture of impurity scattering[7] the important parameters are the Periodic Table column numbers of impurity and host, Z and Z_0, respectively. The conduction electrons are taken to be scattered by a spherical square-well potential whose depth is determined self-consistently from the well-known Friedel sum rule which relates $Z - Z_0$ to a sum over phase shifts of the various scattered partial waves. In this way one is calculating the simple Coulomb scattering arising from the difference in nuclear charge on solute and solvent, $Z - Z_0$, screened self-consistently by the conduction-electron assembly.

Now it is clear *a priori* that solute and solvent ions must differ not only in their net charge but also as to the detailed form of their potential, and experimentally, of course, isovalent impurities ($Z = Z_0$) often exhibit considerable scattering. The basic physical question addressed in this paper is: Under what conditions is it possible to represent the effects of these actual differences in potential within the framework of a simple model? The model in question is basically that due to Blatt[2] who noted that a first-order structural difference between solute and solvent ions is simply the difference in their over-all sizes. By insisting on charge neutrality within the volume of the solute ion, the screening charge in the Friedel sum rule becomes $Z - Z_0(1+\beta)$, where β is directly related to the size mismatch between solute and solvent. Since β can be positive or negative the resulting "lattice-distortion screening" can actually increase *or* decrease the scattering.

One then proceeds to calculate the impurity scattering cross section using plane-wave conduction-electron states and thus assigning all electrons at the Fermi surface the same wave vector k_F. The effects of host band structure are then subsumed in a quantity n_{eff} which represents the effective number of "free" conduction electrons per atom and which is treated as a parameter to be varied to give a best fit to the data for each solvent. In terms of the quantities defined above, the model gives the following expression for the residual resistivity per atomic percent impurity $\Delta\rho$:

$$\Delta\rho = \frac{1}{k_F n_{\text{eff}}} F(Z,\ Z_0,\ \beta)\ , \qquad (1)$$

where the model allows one to calculate the functions $F(Z,\ Z_0,\ \beta)$. In the numerical work F was calculated for all combinations of Z(0 through 5) and Z_0(1 through 4) for each combination taking β values over the range $-1 < \beta < 2$.

The "extension" of the original Blatt model which the above treatment represents consists mainly of treating n_{eff} as a disposable parameter. Of less significance is the fact that the actual evaluation of β is done somewhat differently from the original Blatt work, but the reader is referred to Ref. 1 for full details on this point. Table I contains the collected pure-metal data for each solvent needed to calculate $\Delta\rho$.

RESULTS

Some new experimental data were obtained for Cd alloys in the course of this study which seem to offer a particularly clear-cut example of the utility of Blatt's model. Accordingly we shall

TABLE I. Properties of pure metals employed in the present work.

			n_{eff}	
Metal	k_F (a.u.)	Poisson's ratio	Present study	Other studies
Be	1.028	0.03[a]	0.20	0.34[e]
Mg	0.727	0.35[b]	0.59	1.20[f]
Zn	0.835	0.25[b]	0.60	0.82[f]
Cd	0.747	0.28[c]	0.76	0.78[f]
Al	0.927	0.36[b]	1.19	2.18[g]
In	0.797	0.33[d]	0.70	···
Sn	0.864	0.33[a]	0.26	1.12[g]
Pb	0.836	0.43[a]	0.14	1.24[g]

[a] *Metals Reference Book*, 4th ed., edited by C. J. Smithells (Plenum, New York, 1967).

[b] *A.I.P. Handbook*, 2nd ed. (McGraw-Hill, New York, 1963).

[c] An estimate based on known elastic constants for cadmium.

[d] Since no value appears to be available for indium, the value for the neighboring element in the Periodic Table (Sn) was adopted.

[e] Based on calculations shown by J. H. Tripp, P. M. Everett, W. L. Gordon, and R. W. Stark, Phys. Rev. 180, 669 (1969).

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TABLE II. Experimental and calculated residual resistivities, ρ_{expt} and ρ_{calc}, for dilute cadmium alloys ($\mu\Omega$ cm/at. %).

Impurity	ρ_{expt}	ρ_{calc}
Cu	0.28 ± 0.03	0.26
Ag	0.33 ± 0.02	0.53
Au	0.70 ± 0.03	0.53
Mg	0.31 ± 0.02[a]	0.00

[a] R. S. Seth and S. B. Woods, Phys. Rev. B 2, 2961 (1970).

present them in more detail than is necessary for our more extensive survey.

a. Cadmium alloys. Table II records the results. The experimental data were obtained by entirely conventional means, the only problem being presented by the case of *Cd*Cu since the maximum solubility of Cu is no more than 0.1 at.%. The values presented in the table were obtained by averaging over the following number of alloy samples with more or less equally spaced impurity concentrations up to the maximum indicated: *Cd*Cu (4, up to 0.1 at.%), *Cd*Ag (7, up to 1.25 at.%), *Cd*Au (4, up to 0.5 at.%). The parameter n_{eff} recorded in Table I for cadmium was obtained by fitting the data for these solutes to the model. Although the agreement is by no means perfect, the model correctly predicts the surprising result that the resistivity of copper in cadmium is *less* than that of silver. This is a very clear-cut case of substantial lattice distortion actually *reducing* the scattering cross section. Ag is next to Cd in the Periodic Table and hence differences in the actual potential of solute and solvent ions are probably much greater for *Cd*Cu than for *Cd*Ag. However, the effect of these differences is completely masked by the lattice-distortion screening term. The inability of the model to discriminate between Ag and Au as solutes has been discussed in detail in Ref. 1 in the case of zinc as solvent, and Table II serves to demonstrate that a similar situation exists for cadmium. Clearly the *Cd*Mg results are in violent disagreement with experiment, but this is merely a particular example of the general result which will be discussed in the next section. Finally, the best-fit value for n_{eff} is 0.76 which compares very well with the value found from Fermi-surface studies, namely, $n_{\text{eff}} = 0.78$.

b. Extended study. Table III sets out the results of our extended study in the form of values for the ratio $\Delta\rho_{\text{calc}}/\Delta\rho_{\text{expt}}$, where the values of $\Delta\rho_{\text{expt}}$ were obtained from the literature. Combinations above the line have $Z < Z_0$ and below the line $Z \geqslant Z_0$. It is immediately clear that there *is* a good quantitative distinction between the two regimes as far as the applicability of the simple model is concerned. Before proceeding to a discussion of this result it is appropriate to record in this section some details of the construction of Table III: The parameter n_{eff} was adjusted in each case to give a best fit for $Z < Z_0$. However, giving n_{eff} any arbitrary value, a basic quantitative distinction is still maintained between the two regimes mentioned; namely, $\Delta\rho_{\text{calc}}/\Delta\rho_{\text{expt}}$ typically varies by a factor of 2 for $Z < Z_0$ but by *more than an order of magnitude* for $Z \geqslant Z_0$. Further, the values of n_{eff} obtained by fitting to the data for $Z < Z_0$ are recorded in Table I and except for Sn and Pb, are within about a factor of 2 of the values suggested by Fermi-surface studies. Fitting to the $Z \geqslant Z_0$ data would make the n_{eff} values very much smaller and completely destroy this agreement. Our choice of solvents and impurities to include in Table III was governed entirely by the availability of experimental data, which is unfortunately not as extensive or reliable as it might be. Values taken from different references (shown next to the solvents) occasionally differ among themselves by as much as 30% for $\Delta\rho_{\text{expt}}$, and in those cases a simple average value was adopted. For these reasons, however, even where we believe the model itself to provide a reliable estimate for the resistivity, namely, for $Z < Z_0$, the ratio $\Delta\rho_{\text{calc}}/\Delta\rho_{\text{expt}}$ can only be regarded as meaningful to the two significant figures recorded in the table. Finally, the impurity nickel was treated as having valence zero, i.e., as contributing no electrons to the conduction band. Although this procedure might be thought to be rather dubious, the fact that it actually works quite well provides further support for the point of view we shall outline in the next section.

DISCUSSION

Our suggestion to account for the change in behavior around $Z = Z_0$ is a simple one. For $Z < Z_0$ the impurity represents a *repulsive* scattering potential, while for $Z > Z_0$ the potential is *attractive*. It is clear that true differences in the structure of solvent- and impurity-ion cores are highly localized within the core itself and can contribute to the scattering only to the degree that the conduction electron penetrates the core region. For a repulsive potential the electron is kept away from the core so in that case one might expect that the scattering would be relatively insensitive to the short-range details of the scattering potential. On this view, then, the major portion of the observed resistivity for $Z \geqslant Z_0$ in the systems studied derives from short-range details of the potential in the core, whereas the long-range Coulomb potential outside the core is responsible for the scattering when $Z < Z_0$.

It is natural to inquire, at this point, whether

TABLE III. Values of the ratio ρ_{calc}/ρ_{expt} for polyvalent alloys.

Solute	Solvent Be Ref. (a, b)	Mg (c, d, e)	Zn (f, g)	Cd (h)	Al (c, i, j)	In (k, l, m)	Sn (n, o)	Pb (k, p, q)
Ni	1.1				0.9			
Li		1.3			1.6			
Cu	0.9		1.6	0.9	1.0			
Ag		0.9	1.2	1.6	1.0			
Au			0.8	0.8				
Be								
Mg				0.0	1.4			0.9
Zn					0.7		0.8	
Cd		0.0	0.6		1.0	1.0	1.3	1.0
Hg		0.0	0.4			1.0		2.0
Al		0.9	1.3					
Ga					0.1	0.7		
In		0.2	0.1				1.0	0.4
Tl		0.1				0.0		1.1
Si					0.1			
Ge					0.0			
Sn		0.4	0.2			0.7		1.5
Pb		0.3			0.0	0.3	0.3	
Sb							0.5	1.2
Bi		0.3					0.1	0.1

[a] A. P. Klein and A. J. Seeger, J. Appl. Phys. 37, 1346 (1966).

[b] J. Lawson (private communication).

[c] F. Pawlek and K. Reichel, Z. Mettallk. 12, 1 (1958).

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[e] F. J. Blatt, *Physics of Electronic Conduction in Solids*, 1st ed. (McGraw-Hill, New York, 1968).

[f] Reference 1.

[g] Reference 6.

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[o] P. Alley and B. Serin, Phys. Rev. 116, 334 (1958).

[p] Reference 3.

[q] J. D. Livingston, Phys. Rev. 129, 1943 (1963).

such a view is consistent with work which has attempted to go beyond the evident limitations of the model set out here. There are two pieces of evidence that this is the case. In the first place, Daniel and Léonard[8] investigated the effect of changes in the form of the scattering potential on the calculated results, within the framework of a free-electron model, and found very much more drastic changes for $Z > Z_0$ than for $Z < Z_0$. Secondly, employing a pseudopotential formalism, Fukai[9] showed that in the case of aluminum as a solvent, the calculated resistivity was about five times more sensitive to changes in ion-core radius for $Z \geqslant Z_0$ than it was for $Z < Z_0$. This result was obtained using two plane waves instead of just one, and encourages the view that it will emerge as a feature of any calculation.

Finally, in the light of the preceding paragraphs it will be recalled that Blatt's model was successful for the noble-metal solvents[2] despite the fact that for all impurities there considered, Z was greater than or equal to Z_0, i.e., all impurities represented an attractive potential. It is not immediately obvious what distinguishes the noble-metal solvents from the polyvalent hosts. However, two points should be mentioned. First, the success of the model is not complete. It predicts that the Au-row solutes should scatter *less* than the Ag-row when dissolved in either Ag or Cu. In fact they scatter *more*,[10] an indication that short-range aspects of the ion-core structure are responsible for a significant share of the scattering in these cases. Second, since the Fermi energy increases with host valency, the penetration of the conduction electrons into the ion cores is least for the noble-metal alloys. This is one factor which may lead to a distinction between the noble-metal solvents and those considered here.

CONCLUSIONS

We have presented the first systematic study of the behavior of the residual resistivity over a very wide range of polyvalent alloy systems. A well-marked regularity has emerged which has suggested that a physical distinction exists between two types of scattering in such alloys. If Z and Z_0 are the impurity and solvent valencies, respectively, then for $Z \geqslant Z_0$ there is a large contribution to the scattering arising from differences of potential deep inside the ion cores. However, for $Z < Z_0$, resistance arises primarily from scattering by the long-range Coulomb potential which can be reasonably approximated within the framework of existing simple models.

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Effect of Pressure on the Interstitial Diffusion of Nickel in Lead to 50 kbar*

C. T. Candland and H. B. Vanfleet
Brigham Young University, Provo, Utah 84601

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The diffusion of nickel in lead has been investigated using radioactive-tracer and sectioning techniques for pressures of up to 50 kbar and for temperatures in the range 208–591 °C. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation energy and preexponential factor. The activation energy and volume at the melting temperature and atmospheric pressure are, respectively, $\Delta H = 10.6 \pm 0.4$ kcal/mole and $\Delta V/V_0 = 0.13 \pm 0.04$. The pressure and temperature coefficients of the activation volume, although quite uncertain, were also determined. The small activation energy and volume indicate that nickel diffuses in lead primarily by the interstitial mechanism.

I. INTRODUCTION

The diffusion of the near-noble metals (group IIB and VIIIB elements) in lead has been of interest since the early work of Seith, Hofer, and Etzold,[1] who measured the diffusion of Ni, Cd, and Hg in Pb. This interest stems at least in part from the observation that the diffusivity of these impurities in lead tends to be more rapid than for lead self-diffusion,[2,3] yet much less than for the diffusion of the noble metals in lead.[4] This observation is substantiated by the more recent work of Miller[5] for the diffusion of Cd in Pb and by preliminary measurements at this laboratory for Pd in Pb. Furthermore, a number of similar bimetallic systems have been found which also exhibit unusually rapid diffusion. These include Cu, Au, Zn, and Ag in Sn; Au and Ag in In and Tl; Au and Co in Pr; and Cu, Au, Na, Zn, and Ag in Li.[6] The basic question one would like to answer is in regard to the respective mechanisms of diffusion for these rapidly diffusing systems.

Recent high-pressure measurements for self-diffusion[7,8] and for impurity diffusion of the noble metals[9–11] in Pb have helped to establish the respective diffusion mechanisms involved. By applying kinetic theory and equilibrium thermodynamics, an activation volume ΔV is obtained through the pressure dependence of the diffusion coefficient. For interstitial diffusion ΔV involves only the activation volume of motion ΔV_m of the impurity ion, whereas for substitutional diffusion ΔV includes both an activation volume of motion ΔV_m and an activation volume of vacancy formation ΔV_f. Theoretical estimates[12,13] for ΔV_m and ΔV_f are < 0.2 and 0.55 atomic volumes, respectively. These estimates are in good agreement with the experimental values for ΔV_m and ΔV_f of 0.15 and 0.53 atomic volumes as obtained from high-pressure annealing[14] and quenching[15] experiments in Au. One further finds excellent correlation for the measured activation volume $\Delta V_m + \Delta V_f$ of 0.64–0.72 atomic volumes as obtained from measurements of the pressure dependence of Pb self-diffusion.[7,8]

The measured activation volumes for the diffusion of Cu, Au, and Ag in Pb are 0.04, 0.28, and