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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 Blatt¹ 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

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

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 Mott⁴ 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. Solute 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 Frankhouse⁶ on

aluminum alloys, we may mention the work of Green⁷ on the resistivity of liquid alkali alloys and also of Hurd and Gordon⁸ on many properties of noble-metal alloy systems. On the other hand, impurity scattering might be expected to depend upon the details of the ion core potential. The degree to which a lattice-distortion model can be expected to represent these details has often been questioned and it has been suggested that simple size-effect considerations may be inadequate.⁹ It is thus of some interest to see whether any evidence on this point can be extracted from our new data.

EXTENDED BLATT MODEL

The Friedel treatment of electron scattering by the solute atoms in an alloy regards them as independent scattering centers embedded in a host lattice where the potential seen by a conduction electron is otherwise constant. Under these conditions the phase shifts η_l of the partial waves arising from the plane wave solutions of Schrödinger's equation in the pure solvent must satisfy the Friedel sum rule

$$\delta Z = (2/\pi) \sum_{l=0}^{\infty} (2l+1) \eta_l, \quad (2)$$

if δZ is the net charge to be screened by the conduction electrons at each solute atom site. The phase shifts depend on the energy or wave number of the electrons, but for the Friedel sum, the only electrons involved are those at the Fermi level with wave vector of magnitude k_F . These phase shifts give rise to a total scattering cross section σ for each atom, given by

$$\sigma = \frac{4\pi}{k_F^2} \sum_{l=0}^{\infty} (l+1) \sin^2(\eta_l - \eta_{l+1}). \quad (3)$$

To obtain the resistivity, we use σ to define an isotropic relaxation time in the Boltzmann equation, which for small electric fields gives the current flow by an integration over the Fermi surface. The familiar result for the residual resistivity in $\mu\Omega\text{cm/at.}\%$ is

$$\Delta\rho = 2.732 \frac{1}{k_F n_{\text{eff}}} \sum_{l=0}^{\infty} (l+1) \sin^2(\eta_l - \eta_{l+1}), \quad (4)$$

if k_F is in a.u. n_{eff} is the effective number of conduction electrons assumed by each solvent atom which, with certain assumptions, is given by an expression of the form

$$n_{\text{eff}} = Z_0 3 \langle \int \cos^2 \theta dS \rangle / S_F \quad (5)$$

in which θ is the angle between the applied field and the velocity of an electron at the Fermi surface S , while S_F is the area of the free-electron sphere. $\langle \rangle$ denotes angular averaging. For a free-electron metal, n_{eff} reduces to Z_0 which in

the noble-metal alloys is just unity.

Blatt's model differs from Friedel's only in the value taken for δZ in Eq. (2). Whereas Friedel took $\delta Z = \Delta Z$, Blatt, following Harrison,¹⁰ argued as follows: If V_0 is the volume occupied by a solvent ion, then the solute ion volume is $V = V_0(1+\beta)$, where β is the fractional difference between V and V_0 . The average conduction charge density in the host is Z_0/V_0 so that the host can provide $Z_0(1+\beta)$ electrons in the volume of the solute ion to help screen the Z positive charges there. This leaves $\delta Z = Z - Z_0(1+\beta)$ positive charges to be screened by modification of the (free-) electron gas. The values of β to be used in finding δZ were obtained for the noble metal alloys from lattice-spacing data and the relationship

$$\beta = (1+\nu)/(1-\nu) \delta a/a, \quad (6)$$

where ν is Poisson's ratio and $\delta a/a$ the change in lattice parameter in percent per atomic percent solute. This expression arises from considering the lattice as an isotropic elastic continuum.¹¹

To calculate the η_l required in Eq. (2), Blatt took advantage of the insensitivity of $\Delta\rho$ to the solute potential adopting a square well with a radius obtained from V and a depth adjusted to satisfy Eq. (2). In this form, the phase-shift calculation is particularly simple (see, e.g., Schiff¹²).

There are three points which must be examined before we can apply this model to a polyvalent solvent, such as zinc. First, the calculation of β in Eq. (6) is based on the isotropic elastic continuum approximation. The elastic moduli for zinc do exhibit anisotropy (about twice as great as for the noble metals) but we follow Blatt in adopting a value of ν obtained for the polycrystalline solvent.

Another difficulty associated with Eq. (6) is due to the pressure exerted by the conduction electron gas. A theory due to Jones¹³ for the lattice spacings in cph metals asserts that they are largely determined by the occupancy of conduction states and that the solute size factor is unimportant. Hence, lattice-spacing data cannot be used to calculate β unless the electronic effect is first subtracted out. As the electronic contribution is not known with confidence, we have adopted a different estimate of β , namely,

$$\beta = \frac{1}{3} [(1+\nu)/(1-\nu)] (\delta V/V_0), \quad (7)$$

where $\delta V = V - V_0$ is deduced from the pure metal atomic volumes. In this form, the result is the same as for the elastic spherical inclusion problem. For noble metal alloys, both Eqs. (6) and (7) give similar β values. We have repeated Blatt's calculations and confirmed that the rms deviation of the resistivity from experiment is practically

unaltered by using Eq. (7) in place of Eq. (6).

Last, although a free-electron model for scattering in zinc seems reasonable in view of what is known of the Fermi surface, it is clear from Eq. (5) that n_{eff} is not particularly easy to calculate and it was thus treated as a parameter to be found by fitting to all our data. We then investigate how well this one-parameter model accounts for experimental results.

CALCULATION

We have used the same model as Blatt, taking the solute potential to be a square well whose depth is adjusted to satisfy Eq. (2). In this form one finds that the η_i depend on the Fermi radius k_F only through the combination $k_F r_s$ where r_s is the solvent atomic radius, and this combination depends only on Z_0 . The solute atom is characterized by β and Z , so that Eq. (4) can be written

$$\Delta\rho = (1/k_F n_{\text{eff}}) F(Z, Z_0, \beta), \quad (8)$$

where F is a universal function. For Zn alloys, we obtain β from Eq. (7) using $\nu = 0.25$,¹⁴ while atomic volumes are obtained from the bulk densities.¹⁵ The Fermi radius is $k_F = 0.835$ a. u. and $Z_0 = 2$. In Fig. 1 the family of F curves for $Z_0 = 2$ is displayed as a function of β and for various values of Z . The model predicts $\Delta\rho = 0$ when $\delta Z = 0$, i. e., when $\beta = Z/Z_0 - 1$, which corresponds to a solute ion whose average valence charge density Z/V is the same as that of the solvent. In this situation the model implies that the ion becomes invisible to the electrons in the alloy. Our least-squares best-fit value of n_{eff} is found to be 0.60 so that the effective number of current carriers is only about a third of the number of available valence electrons. It is interesting that this is the same fraction as that found by Blatt *et al.*⁶ in their treatment of aluminum alloys.

EXPERIMENTAL PROCEDURES

The experimental procedures will not be discussed at length here since the standard four-terminal technique was used, and Matthiessen's rule was applied to extract the residual resistivity from measurements made at 4.2 and 300° K. However, certain precautions, principally metallurgical, were found necessary to ensure accurate and reproducible results and these are discussed in detail elsewhere.¹⁶ The samples, in polycrystalline form, were subjected to a variety of annealing and quenching procedures and from the internal systematics of their behavior it was concluded that homogeneous solutions were available up to at least 4, 1, 1, 0.75, and 0.5 at. % for Au, Ag, Cu, Al, and Cd, respectively. The following al-

loys were examined for Au: 0.25, 0.50, 0.75, 1.00, 2.00, 3.00 and 4.00 at. %; for Ag and Cu: 0.25, 0.50, 0.75, and 1.00 at. %; for Al: 0.25, 0.50, and 0.75 at. %; and for Cd: 0.25 and 0.50 at. %. In Table I we give the average values and average magnitude of the deviation of $\Delta\rho$ for each solute. The residual resistivity per at. % impurity is seen to be experimentally a well-defined number with at most an 8% uncertainty in the case of copper. One other solute, mercury, shows a nonvanishing solubility in zinc. The data for this solute had been obtained in a prior independent study by Fiske¹⁷ who kindly supplied the result in Table I.

DISCUSSION

Previous experimental work on the residual resistivity of zinc-based alloys has yielded curious results. Aleksandrov's studies¹⁸ of the solutes Cd, In, Bi, and Sn in zinc showed a highly nonlinear dependence of the resistivity on concentration. Since this was apparently independent of the solute used and since he observed a similar behavior with cadmium as a solvent, he suggested that it was in some way a property of the hexagonal solvents. Desalvo *et al.*¹⁹ subsequently found a similar nonlinear behavior for the solutes Cu, Cd, and Pb. A cursory inspection of the alloy phase diagrams²⁰ gives a clue to this behavior. All of the solutes mentioned except Cd and Cu show an almost negligible solubility in zinc, and it is therefore possible that simple precipitation effects might well have been responsible for the curious concentration dependencies reported. It was for this reason that the decision was made in this work to examine only those solutes which do have an appreciable ($\sim 1\%$) solubility in zinc. The results presented here have clearly established that, for these

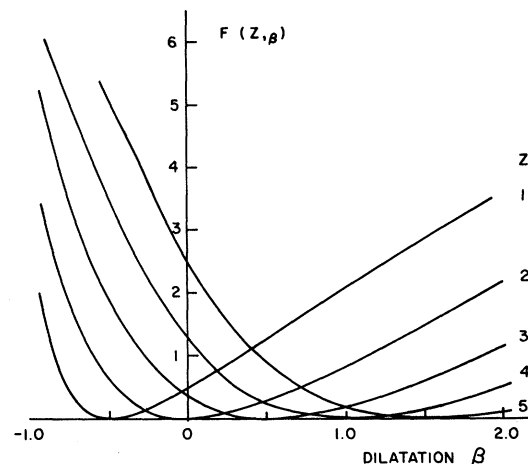


FIG. 1. Universal function $F(Z, Z_0, \beta)$ for $Z_0 = 2$, giving the residual resistivities according to Eq. (8).

TABLE I. Observed and calculated residual resistivities in $\mu\Omega\text{cm/at. \%}$ for dilute zinc alloys. $\Delta\rho_{\text{calc}}$ is obtained using the tabulated value of β while $\Delta\rho_{\text{calc}}(\beta=0)$ is obtained by choosing $\beta=0$.

Solute	β	$\Delta\rho_{\text{expt}}$	$\Delta\rho_{\text{calc}}$	$\Delta\rho_{\text{calc}}(\beta=0)$
Al	0.06	0.40 ± 0.02	0.50	0.71
Cd	0.25	0.25 ± 0.00	0.14	0.00
Hg	0.33	0.56 ± 0.03	0.24	0.00
Cu	-0.13	0.38 ± 0.03	0.60	0.87
Ag	0.07	1.00 ± 0.02	1.20	0.87
Au	0.07	1.46 ± 0.06	1.20	0.87

solutes at least, the residual resistivity per at. % impurity is a well-defined experimental quantity.

A comparison of the experimental and theoretical values using $n_{\text{eff}} = 0.60$ is made in Table I. In order to exhibit the contribution from the lattice distortion, also included in this table are the values of $\Delta\rho$ calculated by setting $\beta = 0$. These depend only on the solute valency. It is at once clear that including the effects of lattice distortion through our value of β [Eq. (7)] significantly increases agreement between theory and experiment. At the same time however one can see that lattice distortion does not account completely for the variations in the effect of different solutes.

Perhaps the most serious qualitative failure of the model is its inability to make any distinction between Ag and Au. Since these solutes have practically the same atomic volumes, Eq. (7) gives identical estimates for the lattice distortion and the model therefore predicts the same $\Delta\rho$, whereas experimentally Au evidently possesses a considerably higher scattering cross section than silver. Furthermore, although Eq. (7) is an admittedly crude representation of the distortion, an independent argument gives us some confidence that the local strains due to silver and gold are very similar. The observed atomic volume changes produced by alloying zinc with Ag and Au are identical.²¹ Since these solutes are isovalent, changes in atomic volume deriving from electronic structure effects should be very similar. Hence the lattice-spacing data themselves allow us to conclude that Ag and Au produce very nearly the same local strain in zinc. A simple lattice distortion model therefore appears unable to account for the resistivity difference observed between Ag and Au. On the other hand the difference between Cu and Ag is quite nicely accounted for, as indicated in Table I. The question arises whether these distinctions between Cu, Ag, and Au as solutes appear solely in the case of zinc as a solvent or are perhaps more general. Collected together in Table II are experimental data on $\Delta\rho$ differences in all the nontransition-element solvents we could find which dissolve more than one of the noble metals. These observed differences are compared

with the predictions of Blatt's model (in parenthesis). A study as extensive as the present work is unfortunately not feasible for Cd-based alloys since very few metals display an appreciable solubility in Cd and in particular Cu is reported to have an essentially zero solubility.²⁰ The Cd data recorded in Table II was obtained in an unpublished study in this laboratory and the Al and noble-metal results were all obtained from Blatt's work.^{1,6} The column headed $\Delta\rho[\text{Ag-Cu}]$ contains the experimental (calculated) differences between the residual resistivity in $\mu\Omega\text{cm}$, of 1% of Ag and Cu in each solvent and similarly for the column headed $\Delta\rho[\text{Au-Ag}]$. Without exception, it can be seen that although $\Delta\rho[\text{Ag-Cu}]$ varies substantially in magnitude and even sign, it is reasonably well accounted for by the model. However the experimental value for $\Delta\rho[\text{Au-Ag}]$ has a remarkably constant magnitude of ~ 0.4 but remains completely unaccounted for. Our conclusion from Table II is that the differences between the behavior of Cu, Ag, and Au as solutes are indeed quite general and must reflect a fundamental difference in the response of conduction electrons to these ion cores. It is tempting to suggest that the unexpectedly large scattering cross section for gold may be due to the fact that it is the only noble metal to possess a shell of f electrons in the core. The present model can make no explicit allowance for symmetry effects but from the point of view of a pseudopotential model it is likely that the existence of a symmetry difference between the solute and solvent core states may provide an additional contribution to the scattering. Further, if such a contribution exists, one would expect the model to systematically underestimate the resistivity for Hg as a solute. As can be seen from Table I, Hg in Zn does indeed have a larger resistivity than expected, and, in fact, Hg and Au are the two solutes whose experimental resistivities exhibit the greatest numerical deviation from the model predictions. An examination of the suggested origin for this behavior would take us far outside the

TABLE II. Experimental (calculated) differences between the resistivity of silver and copper, $\Delta\rho[\text{Ag-Cu}]$, and between gold and silver, $\Delta\rho[\text{Au-Ag}]$, in all non-transition-element solvents which dissolve more than one noble metal. Values are in $\mu\Omega\text{cm/at. \%}$.

Solvent	$\Delta\rho[\text{Ag-Cu}]$	$\Delta\rho[\text{Au-Ag}]$
Cu	0.14 (0.11)	0.41 (0.03)
Ag	-0.14 (-0.06)	0.36 (0.00)
Au	-0.09 (-0.08)	-0.36 (0.00)
Zn	0.62 (0.60)	0.46 (0.00)
Cd	...	0.40 (0.00)
Al	0.50 (0.65)	...

framework of the present model. However, the suggestion that has been made does seem to offer a plausible qualitative explanation for the systematic character of the discrepancies identified in both Tables I and II.

In summary, it has been shown that the inclu-

sion of lattice distortion much improves agreement between experiment and theory for the residual resistivity of zinc alloys. Thus, although systematic discrepancies have been identified and discussed, we conclude that significant lattice-distortion screening occurs in zinc-based alloys.

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Effect of Thermal Umklapp on the Low-Temperature Electrical Resistivity

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The Klemens-Jackson theory of the low-temperature resistivity of those monovalent metals whose Fermi surface touches or nearly touches the Brillouin-zone boundary has been extended to include the presence of impurity scattering, which is described by an isotropic relaxation time. The electrical resistivity thus obtained is in the form of a slowly converging infinite series. The deviations from Matthiessen's rule which occur as a consequence of the simultaneous presence of thermally induced umklapp processes and impurity scattering are calculated. They prove to be large and have a temperature dependence that, over limited temperature intervals, could be spuriously interpreted as showing evidence of electron-electron scattering.

In recent years, there has been considerable interest in the temperature dependence of the electrical resistivity at low temperatures. This interest has arisen because the low-temperature

electrical resistivity can, in principle, indicate the presence or absence of certain electron-electron interactions. Baber scattering,¹ spin density fluctuation scattering,² and magnon scattering³ can be