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First-Principles Calculation of the Residual Electrical Resistivity of Random Alloys

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Results of numerical calculations of the electrical resistivity of the following primary solid-solution alloys are presented: Cu(Zn), Cu(Ga), Cu(Ge), Ag(Pd), and Ni(Mo). Our theoretical model is one reported earlier by Butler and uses a charge-self-consistent Korringa-Kohn-Rostoker coherent-potential approximation. The calculations are valid for strong as well as weak scattering, and for the first time, vertex corrections are included. Excellent agreement is obtained with experiment for the resistivity.

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We report here rigorous and realistic *ab initio* calculations of the dc residual resistivity of random substitutional alloys. The calculations do not use adjustable parameters and they start with only the atomic numbers, the alloy concentrations, and the lattice parameters as input.[1] The model is based on the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA)[2] and the one-electron Kubo formula.[3] It goes beyond any previous model for determination of transport properties of random alloys in that it is not limited to weak scattering and does not require the existence of well-defined quasiparticles. We believe that the model is valid in the regime where the Boltzmann equation breaks down because energy bands are not defined. The model includes vertex corrections, and it properly treats the momentum matrix elements. In this paper we discuss our results for copper-rich alloys of zinc, gallium, and germanium, for silver alloys containing palladium, and for nickel alloyed with molybdenum.

The dc electrical conductivity tensor in the one-electron approximation can be written in the Kubo formalism as[1]

$$\sigma_{\mu\nu}(\epsilon)=\frac{2\hbar}{N\Omega\pi}\lim_{\substack{\eta\to 0\\ \eta'\to 0}}\int d^3r\int d^3r'[j_\mu \operatorname{Im}G(\mathbf{r},\mathbf{r}',\epsilon+i\eta)][j_\nu \operatorname{Im}G(\mathbf{r}',\mathbf{r},\epsilon+i\eta')], \tag{1}$$

where the current operators are

$$j_\mu=-i\hbar\frac{e}{m}\frac{\partial}{\partial r_\mu},\quad j_\nu=-i\hbar\frac{e}{m}\frac{\partial}{\partial r_\nu'}. \tag{2}$$

For a spherical nonoverlapping muffin-tin potential, the imaginary part of the Green's function can be expressed as[4]

$$\begin{aligned}&\operatorname{Im}G(\mathbf{r},\mathbf{r}',\epsilon+i\eta)\\&\quad=\tfrac{1}{2}[\tilde{G}(\mathbf{r},\mathbf{r}',\epsilon+i\eta)-\tilde{G}(\mathbf{r},\mathbf{r}',\epsilon-i\eta)],\end{aligned} \tag{3}$$

$$\tilde{G}(\mathbf{r},\mathbf{r}',z)=\frac{2m}{\hbar^2}\sum\tau_{LL'}^{mm}(z)Z_L^m(\mathbf{r}_m,z)Z_{L'}^n(\mathbf{r}_n',z) \tag{4}$$

for the complex energy z. The point $\mathbf{r}$ is in unit cell m while the point $\mathbf{r}'$ is in cell n with $\mathbf{r}=\mathbf{R}_m+\mathbf{r}_m$, where $\mathbf{R}_m$ is the vector to the center of cell m. (We consider, for simplicity only, one atom per unit cell.) $Z_L^m(\mathbf{r}_m,z)$ is the wave function of angular momentum L $(\equiv l,\mu)$ centered on cell m which is regular at the origin and which satisfies the one-electron Schrödinger equation with the spherical muffin-tin potential and complex energy z. The τ^{mn} is the scattering-path operator which propagates the electron from site m to site n taking into account scatterings at all possible sites.

For a binary alloy of atoms A and B, the potential site n depends on whether it is occupied by an A or B atom. To represent a real random system, we take a configurational average considering all possible arrangements of the two species on the fixed lattice and for the given concentration. We assume that the arrangements are completely random with no short-range chemical order. We then carry out the configurational average within the CPA. The scattering-path operator τ^{nm} for a given configuration is replaced by τ^{cnm} (the scattering-path operator for the CPA effective medium) plus correction terms.

At this point the algebra becomes rather involved, and the reader should see Ref. 1 for details. The conductivity tensor breaks up naturally into $\sigma_{\mu\nu}=\sigma_{\mu\nu}^0+\sigma_{\mu\nu}^1$, where the first term contains all contributions in Eq. (1) in which $\mathbf{r}$ and $\mathbf{r}'$ are in the same cell (i.e., $n=m$), while the second term has all contributions with $\mathbf{r}$ and $\mathbf{r}'$ not in the same cell. These two sets of contributions must be treated in a fundamentally different way in carrying out the configurational average. When $n=m$, the atoms in cells n and m must be the same atom, and $\sigma_{\mu\nu}^0$ has the form

$$\sigma_{\mu\nu}^0\sim\sum_\alpha c^\alpha\tau^{c00}\tilde{J}_\mu^\alpha\,\tau^{c00}J_\nu^\alpha, \tag{5}$$

where the sum is over the two types of atoms, c^α is the concentration of type α (i.e., the probability that the cell is occupied by species α), and J_ν^α is the νth component of the current matrix element for atoms of type α. $\tilde{J}$ is closely related to J.

For the σ^1 term, the atoms in cells m and n are treated as statistically independent. This term is more complicated than the σ^0 term and it also contains the vertex correction:

$$\sigma_{\mu\nu}^1 \sim \sum_\alpha \sum_\beta c^\alpha c^\beta \tilde{J}_\mu^\alpha [1-\chi w]^{-1} \chi \tilde{J}_\nu^\beta . \qquad (6)$$

The deviation of the factor $[1-\chi w]^{-1}$ from 1 gives the vertex correction (or "scattering in" term).

The quantity χ in σ^1 is essentially the Brillouin-zone average of two τ matrices $\tau_{L_1L_2}\tau_{L_3L_4}$. In our calculations up to now we have restricted our angular momentum expansions to $l \leqslant 2$ which means that each L $(=l,\mu)$ takes on nine different values. Thus, at first glance, it appears that we need $9^4 = 6561$ different terms in χ. However, because of the cubic point symmetry of the alloy (leading to selection rules for the J matrix elements), we have $l_4 = l_1 \pm 1$ and $l_3 = l_2 \pm 1$. With the maximum value of l taken as 2, there are 36 possible L_4L_1 or L_2L_3 pairs. Thus χ is a 36×36 matrix with 1296 elements. We have found by further use of symmetry (using a combination of group theory and computer-generated point operations) that the number of elements of χ that must be calculated is no larger than 114. (The remaining elements vanish or are trivially related to the 114 elements.) This reduction is very important because each of these independent elements must be integrated over the $\frac{1}{48}$th irreducible part of the Brillouin zone.

The computer codes that we have developed are built on the KKR-CPA program of Stocks, Temmerman, and Gyorffy.[5] We also use as input self-consistent potentials that have been generated by Stocks and co-workers. The main part of our calculation of the conductivity consists of three parts. First, we calculate the $36 \times 3 \times 2$ current matrix elements (36 L_1L_4 pairs, three Cartesian components of the current vector, and two atom species for a binary alloy). The second part of the calculation consists of calculating the 114 χ matrix elements (and the $\tilde{\mathbf{J}}$ from $\mathbf{J}$) after the CPA convergence. Finally, the various parts are put together and multiplied by the proper factors to get the conductivity σ (both with and without vertex corrections) in the desired units.

Our calculated residual resistivities for the copper and silver alloys are shown in Fig. 1 as the open triangles. The straight lines for the copper alloys are the Nordheim relation,[6] $\rho \propto c(1-c)$, chosen to go through one of the calculated points. The squares indicate experimental data for the copper alloys[7-11] (open squares for cold-worked alloys and closed squares for annealed samples), while the circles are experimental data for Ag(Pd) alloys[12-14] (open circles for cold-worked alloys and closed circles for annealed alloys). The symbols for the experimental values obscure the calculated points (open triangles) for Ag(Pd) at $c=0.1$, 0.2, and 0.3; for Cu(Zn) at $c=0.1$; for Cu(Ga) at $c=0.05$; and for Cu(Ge) at $c=0.033$ and 0.10. That is, for these concentrations, the calculated points fall directly on (to the accuracy of this graph) the experimental points.

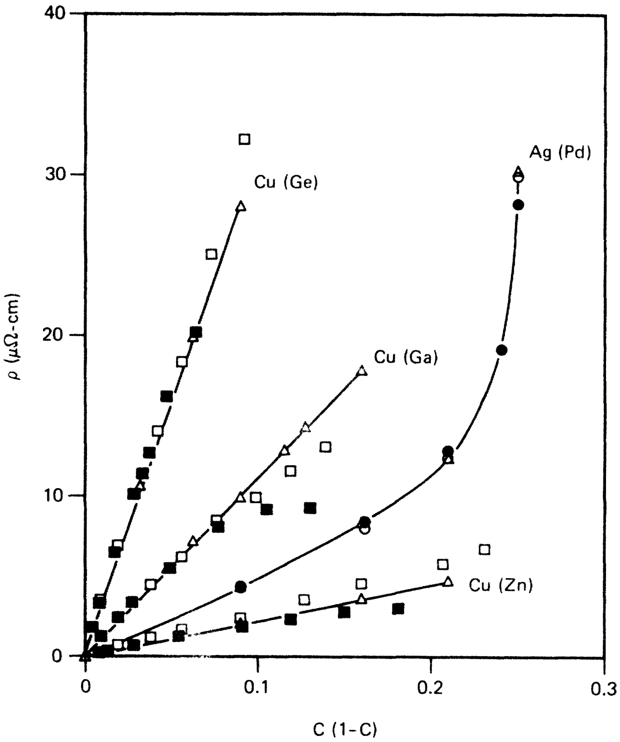

FIG. 1. Calculated and experimental resistivities of Cu(Zn), Cu(Ga), Cu(Ge), and Ag(Pd) alloys. Open triangles are calculated values. The straight lines are the Nordheim relation [$\rho \propto c(1-c)$]. The open symbols [squares for the copper alloys and circles for Ag(Pd)] are for cold-worked samples, while the closed symbols are for annealed samples. The solid line for Ag(Pd) is a guide for the eye. For Ag(Pd) the calculated results at $c=0.1$, 0.2, and 0.3 are obscured by the measured values.

Both the calculated and measured resistivities of the copper alloys follow the Nordheim relation (a straight line) to a good approximation. Experimental results are shown for both annealed[7-10] and cold-worked alloys.[7,11] The experimental and calculated results are in excellent agreement for low concentrations, but near the boundary of the single-phase region ($c=0.38$ for Zn, $c=0.19$ for Ga, and $c=0.085$ for Ge), the measured resistivities of the annealed alloys are lower than the calculations. We attribute this discrepancy to the presence of short-range order in these alloys. When the short-range order is disrupted by cold working, the resistivity increases and in most cases lies slightly above the calculated values. The cold working not only shuffles the atoms, which is desirable from the point of view of comparison with theory since it makes the atomic configuration more disordered, but it also introduces defects such as dislocation which can scatter electrons and cause an increased resistivity.

The main differences between Cu(Zn), Cu(Ga), and Cu(Ge) is that for equal concentrations, gallium scatters more strongly than zinc and germanium more strongly than gallium. This is in qualitative agreement with Linde's "law" which states that the scattering rate for different impurities in the same host should vary as $(\Delta Z)^2$, where ΔZ is the difference in the number of valence electrons of the host and impurity atoms.[15] It may be seen both from the calculations and from the experimental data, however, that the resistivity increases substantially faster than predicted by Linde. The observed ratios of the resistivity per impurity atom of Zn, Ga, and Ge in Cu are approximately 1:5:14 compared to 1:4:9 which would be predicted by Linde's "law."

The calculated and experimental[12-14] resistivity values for the Ag(Pd) alloys are in good agreement. Both deviate strongly from the Nordheim relation for concentrations of palladium greater than about 20%. The detailed physical explanation for this deviation is somewhat complicated but is related to the presence of the palladium d states which contribute the dominant part of the Fermi-energy density of states for palladium concentrations greater than 0.5. Cold work has a much smaller effect on Ag(Pd) alloys than on the copper alloys. Interestingly, cold work causes an initial decrease in the electrical resistivity for palladium concentrations less than 0.5.[14]

For all of the alloys in Fig. 1, the vertex corrections are quite important. For Cu(Zn), Cu(Ga), and Cu(Ge) the effect of including the vertex corrections in the calculations was to reduce the resistivity by factors of approximately 2.51 ±0.01, 2.4 ±0.1, and 2.1 ±0.05, respectively. Under the assumption of weak scattering, the ratio of the resistivity with no vertex corrections to that with vertex corrections can be estimated from the phase-shift differences between the two alloy constituents by[16]

$$\frac{\rho_{\mathrm{NVC}}}{\rho}=\frac{\sum_{l=0}(2l+1)[\sin(\delta_l^A-\delta_l^B)]^2}{\sum_{l=0}(l+1)[\sin\{(\delta_{l+1}^A-\delta_{l+1}^B)-(\delta_l^A-\delta_l^B)\}]^2} \qquad (7)$$

(weak scattering), and this gives, for example, a value of 3.7 ±0.01 for all three concentrations of Cu(Zn). This is quite a bit larger than the value obtained from the more rigorous calculation. [We have checked that our programs give the same results as Eq. (7) in the weak-scattering limit by doing the calculations for small spherical-square-well potentials.]

The effect of the vertex corrections is much smaller in the Ag(Pd) alloys and decreases with increasing palladium content. For $\mathrm{Ag_{0.8}Pd_{0.2}}$ the vertex corrections reduce the calculated resistivity by 24%, while for $\mathrm{Ag_{0.5}Pd_{0.5}}$ the reduction is only 11%. Preliminary calculations for the Pd-rich alloys indicate that vertex corrections are very small for these alloys ($\sim 3\%$). The reason for the absence of vertex corrections in alloys with predominantly d character at the Fermi energy was explained previously.[17]

The calculations reported here include s, p, and d states. Quantitative calculations for transition-metal alloys (which have a Fermi-energy density of states derived primarily from d orbitals) must await the extension of the KKR-CPA and resistivity codes to include f ($l=3$) states. These extensions which are presently in progress are needed because the current matrix elements [Eq. (2)] have odd parity and couple d states to both p and f states. Omission of the f states may cause an underestimate of the electrical conductivity of a transition-metal alloy by as much as 10%. We have observed errors of this order in calculations of the electrical resistivity of Pd-rich alloys of $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$.

In addition to these noble-metal–based alloys, we have calculated the electrical resistivity of the very resistive alloy $\mathrm{Ni_{0.8}Mo_{0.2}}$. The disorder in this alloy is so strong that the energy bands are smeared over the entire Brillouin zone. The resistance of an annealed sample of $\mathrm{Ni_{0.8}Mo_{0.2}}$ decreases significantly when it is cold worked. We attribute this decrease to the disruption of short-range order. Measurements of the resistivity as a function of deformation (reduction in area)[18] indicate that the room-temperature resistivity decreases from 140 to 120 $\mu\Omega$ cm with a 68% reduction in cross-sectional area. With greater deformations the resistivity increases slightly. Since $d\rho/dT$ for $\mathrm{Ni_{0.8}Mo_{0.2}}$ is approximately constant at 0.011 $\mu\Omega$ cm/K below room temperature,[19] the experimental $T=0$ resistivity in the cold-worked state is approximately 117 $\mu\Omega$ cm, in essentially perfect agreement with the calculated value of 116 $\mu\Omega$ cm. Such perfect agreement may be partially fortuitous, however, since defects introduced by cold working probably contribution a few micro-ohm centimeters to the experimental resistivity. The omission of f states, on the other hand, probably increases the calculated resistivity by an amount of the same order so that if both effects were taken into account, excellent agreement between theory and experiment should remain.

The residual electrical resistivities of five random alloys have been calculated from first principles by use of the KKR-CPA and the theory of Ref. 1. No adjustable parameters were used. The agreement between theory and experiment appears to be within the uncertainty associated with inferring the resistivity of random alloys from measurements on real ones. The extension of the theory of Ref. 1 to include short-range order would be very useful.

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