KUBO AND BOLTZMANN ELECTRICAL RESIDUAL RESISTIVITIES OF DISORDERED TRANSITION-METAL ALLOYS

J. Banhart, R. Bernstein, J. Voitländer

Institut für Physikalische Chemie der Universität München

Sophienstr.11, 8000 München 2, FRG

P. Weinberger

Institut für Technische Elektrochemie der Technischen Universität Wien

Getreidemarkt 9, 1060 Wien, Austria

The electrical residual resistivity of the Cu–Pt alloy system was calculated in the framework of the fully relativistic KKR-CPA. Both the linearised Boltzmann equation in the relaxation-time approximation and the one-electron Kubo formula (neglecting vertex corrections) were used to derive the electrical residual resistivity (T=0) from the one-electron Green function of the disordered system. Comparison of the results yielded by the two formulae reveals a very good agreement for the Cu-rich alloys where the complex energy bands are well defined and a discrepancy for the Pt-rich alloys which do not show this feature.

1. INTRODUCTION

The Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA) has been used for calculating quite a number of physical properties of disordered alloys. Beside equilibrium properties such as the density of states or the nuclear spin-lattice relaxation rate the calculation of (non-equilibrium) transport properties is of great interest. Using a simple version of the Boltzmann equation the electrical conductivity σ (or residual resistivity ρ) for zero temperature [4,3] and other transport properties have been calculated for transition-metal alloys. Although the results of the calculations agree quite well with experiments it is not easy to say something about the effect of the two rather crude approximations made for the application of the Boltzmann equation to transport effects: The relaxation-time approximation and the assumed existence of a dispersion relation in the alloy i.e. the existence of well defined complex energy bands. In order to help to clarify this we applied the KKR-CPA form of the Kubo formula for the electrical conductivity (which does not suffer such approximations) to the Cu-Pt alloy system for which calculations based on the Boltzmann equation have already been made [3]. We neglected the vertex corrections in the Kubo formula which

are also absent in the simple version of the Boltzmann equation. So we can study if the assumption of well defined energy bands is valid in this system.

2. THE BOLTZMANN EQUATION

The electrons are treated in a semiclassical manner as wave packets with a wave vector $\vec{k}$ and a spatial position $\vec{r}$, but obeying the quantum mechanical Fermi statistics. The semiclassical equations of motion in an external electric field $\vec{E}$ hold [1]: $\frac{d}{dt}\vec{r} = \vec{v}(\vec{k}) = \frac{1}{\hbar}\vec{\nabla}_k \epsilon(\vec{k})$ and $\frac{d}{dt}\vec{k} = -\frac{e}{\hbar}\vec{E}$. The linearised Boltzmann equation [7] is applied to these electrons. Making use of the relaxation-time approximation the electrical conductivity σ (resistivity ρ) at T=0 for a cubic system is [7]:

$$\sigma = \frac{1}{\rho} = \frac{2}{3}\frac{e^2}{\hbar}\frac{1}{(2\pi)^3}\iint_{FS} \underbrace{\tau(\vec{k}_F)v(\vec{k}_F)}_{l(\vec{k}_F)}\, dS \qquad (1)$$

where τ is the quasiparticle relaxation-time (equal to the transport lifetime in the relaxation-time approximation), v the Fermi velocity and l the mean free path of the quasiparticles. The integration is over the Fermi surface (FS). The mean free path can be calculated from the k-dependent Bloch spectral functions $A_B(\vec{k}, \epsilon_F)$ and is just the inverse of the halfwidth of the Lorentzian peaks in A_B defining the complex energy bands [4,3].

The Lorentzian shape of A_B is due to the simple exponential decay of the k-states described by the relaxation time τ. In case the Fermi surface has more than one sheet (i.e. A_B has more than one peak in certain directions) the electrical conductivity σ is a sum of the contributions of each sheet.

3. THE KUBO EQUATION

The electrical conductivity is given by a configurational average of the product of two single-particle Green functions and the electrical current operators:

$$\sigma_{\mu\nu} = \mathrm{Tr}\langle J_\mu G J_\nu G\rangle_{\text{conf.}}; \quad \mu,\nu \in \{x,y,z\}$$

The average is over all possible configurations of the system. The CPA approximation involves the calculation of a single averaged Green function $\langle G\rangle_{\text{conf.}}$. Butler [5] showed how to use this Green function to calculate the Kubo conductivity of disordered systems. Neglecting the vertex corrections the result for a cubic system is:

$$\sigma = \frac{1}{4}[\tilde{\sigma}(\epsilon^+,\epsilon^+) + \tilde{\sigma}(\epsilon^-,\epsilon^-) \qquad (2)$$
$$-\tilde{\sigma}(\epsilon^+,\epsilon^-) - \tilde{\sigma}(\epsilon^-,\epsilon^+)]$$

where the complex energies ϵ^+ and ϵ^- are defined in terms of the Fermi energy ϵ_F:

$$\epsilon^+ = \epsilon_F + i\eta; \quad \epsilon^- = \epsilon_F - i\eta; \quad \eta \to 0$$

and

$$\tilde{\sigma}(\epsilon_1,\epsilon_2) = \frac{-4m^2}{3\pi\hbar^3\Omega_{\text{at.}}}\left[\frac{1}{\Omega_{\text{IBZ}}}\int_{\text{IBZ}} d^3k \sum_\mu \sum_{\alpha,\beta} c^\alpha c^\beta \qquad (3)\right.$$
$$\mathrm{Tr}\left\{\tilde{J}^{\alpha,\mu}(\epsilon_2,\epsilon_1)\tau(\vec{k},\epsilon_1)\tilde{J}^{\beta,\mu}(\epsilon_1,\epsilon_2)\tau(\vec{k},\epsilon_2)\right\}$$
$$+\mathrm{Tr}\left\{\tilde{J}^{\alpha,\mu}(\epsilon_2,\epsilon_1)\tau^{00}(\epsilon_1)\right.$$
$$\left.\left.(J^{\alpha,\mu}(\epsilon_1,\epsilon_2) - \tilde{J}^{\beta,\mu}(\epsilon_1,\epsilon_2))\tau^{00}(\epsilon_2)\right\}\right]$$

Here τ is the CPA scattering-path operator (τ^{00} being the lattice Fourier transform of $\tau(\vec{k})$), J the current operator and $\tilde{J} = D^t J D$, where D is the CPA impurity operator and D^t its transposed operator. Because the integrand in equation 3 is a scalar with the full lattice symmetry (in this case fcc) the integration can be restricted to one irreducible 1/48 of the Brillouin zone (IBZ). The summation indices are $\alpha,\beta \in \{A,B\}$ (atom species) and $\mu \in \{x,y,z\}$ (spatial coordinates). The relativistic angular momentum representation $\Lambda = (\kappa, m_j, l)$ was used for the various operators. In this representation the current operator is:

$$J^{\alpha,\mu}_{\Lambda,\Lambda'}(\epsilon_1,\epsilon_2) = \frac{-e}{m}\int_{\text{WS}} d^3r\, Z^{\alpha'}_\Lambda(\vec{r},\epsilon_1)\left[i\hbar\frac{\partial}{\partial r_\mu}\right]Z^\alpha_{\Lambda'}(\vec{r},\epsilon_2)$$

where $Z^\alpha_\Lambda(\vec{r},\epsilon)$ is the regular solution of the Dirac equation in the potential sphere α for the energy ϵ, quantum number Λ and the spatial coordinate μ. The integration is over the Wigner-Seitz cell (integration over the muffin-tin sphere is not sufficient).

Once the KKR–CPA equations have been solved and τ has been determined the Kubo conductivity (and resistivity) can be calculated. As far as we know this equation has not been applied to real three-dimensional systems yet. It can be shown that equation 1 can be derived from equations 2 and 3 in case a well defined dispersion relation $\epsilon(\vec{k})$ exists [5]. So in this case the Kubo and Boltzmann resistivities should be equal.

4. RESULTS

The relativistic KKR–CPA equations were solved for 8 compositions of the fcc alloy system Cu-Pt (for details see [2],[3]). The CPA scattering path operator was either used to calculate Bloch spectral functions [8] from which the Boltzmann resistivity was calculated [3] or to calculate the Kubo resistivity by means of equations 2 and 3. Technical details of the evaluation of the Kubo formula will be given in a future publication.

The calculated Kubo resistivities are compared to the corresponding Boltzmann values in figure 1. Apparently the agreement is very good for higher copper concentrations whereas for higher platinum concentrations the results are quite different. Now the Cu-rich alloys are exactly those which have very narrow complex energy bands (i.e. $A_B(k,\epsilon_F)$ has a narrow sharp Lorentzian peak). Moreover only one sheet of the Fermi surface is present in the Brillouin zone for this composition. This can be seen from figure 2 where Fermi surface cuts and the halfwidths of the Bloch spectral functions are displayed for the copper rich alloy $Cu_{71}Pt_{29}$. So the agreement of the Boltzmann and Kubo resistivities is to be expected in this case.

For Pt-rich alloys however the situation is different. The Kubo resistivity is larger than the Boltzmann resistivity. For these alloys two or three Fermi surface sheets are present in the Brillouin zone (see figure 2 for Cu_5Pt_{95} and $Cu_{30}Pt_{70}$). In particular, the second sheet along the X-W-K directions is very broad and the peaks in the Bloch spectral function (see [3]) de-
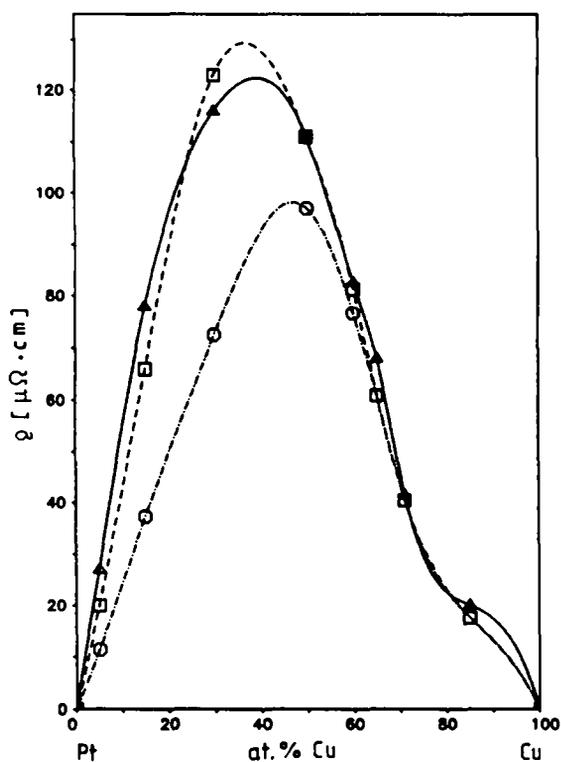
Figure 1: Electrical residual resistivity of Cu-Pt. Triangles: calculated with the Kubo formula; Circles: calculated with the Boltzmann equation; Squares: calculated with the Boltzmann equation neglecting the outer sheets of the Fermi surface. The lines are for better illustration.

Figure 2: Fermi surface cuts of Cu-Pt in the planes Γ-X-U-L-K and Γ-X-W-K. Dots indicate the maxima of the Bloch spectral functions, the contour lines their halfwidth.

viate from the Lorentzian shape making the assumption of sufficiently well defined energy bands questionable. Moreover this relatively complicated situation makes it difficult to evaluate the surface integral in equation 1. Especially near the intersections of the second sheet and the first sheet and near the Brillouin zone boundary the calculation is somewhat ambiguous. Because of the existence of badly defined parts of the Fermi surface and the difficulties with the integration it can be suspected that our application of the Boltzmann equation does not yield the correct contribution to the conductivity for the outer sheets of the Fermi surface. This suspicion is confirmed by comparing the Kubo resistivity to the Boltzmann resistivity arising from the first sheet only (shown in figure 1; the data is from table 1 in ref. [3]). The agreement between these two sets of data is much better. Apparently the contribution of the outer sheets of the Fermi surface is overvalued by the calculation based on the Boltzmann equation.

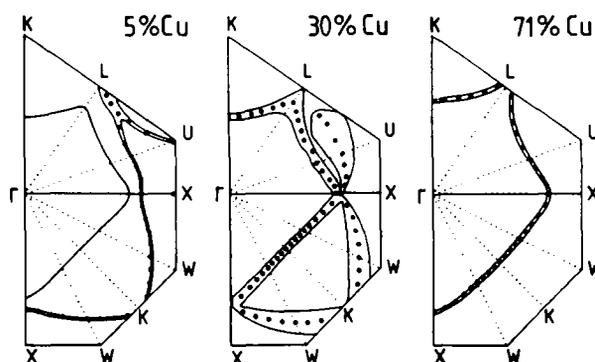Turning to the experimental data it should be noted

that the available room temperature resistivities [6] are closer to the Boltzmann resistivities including the contributions from all sheets of the Fermi surface than to the Kubo resistivities (the experimental results are shown in figure 7 of reference [3]). Therefore the Kubo resistivities do not reproduce the experimental values, especially if one takes into account that the true experimental zero temperature resistivity (low temperature measurements do not yet exist) would be even lower than the available room temperature data. However, one should not forget that even for the calculation using the Kubo formula presented in this paper still many approximations are made: e.g. the vertex corrections are neglected and the alloy potential is not selfconsistent. So the agreement of the experiment with the Boltzmann equation which is better than the agreement with the more sophisticated Kubo equation could be the result of an accidental cancelation of various errors in the calculation based on the Boltzmann equation. Removal of some of these approximations could help to clarify the situation.

5. SUMMARY

The Kubo formula gives the same description of the electrical resistivity as the Boltzmann equation in the relaxation-time approximation when the complex energy bands are well defined. Where this is not the case the Boltzmann equation is not adequate and the Kubo formula should be used.

References

[1] N.W. Ashcroft, N.D. Mermin: *Solid State Physics.* Holt Saunders, 1976

[2] J. Banhart, P. Weinberger, H. Ebert, J. Voitländer: Sol.State Commun. **65**, 693, (1988)

[3] J. Banhart, P. Weinberger, J. Voitländer: J. Phys.: Condens. Matter **1**, 7013, (1989)

[4] W.H. Butler, G.M. Stocks: Phys.Rev. **B29**, 4217, (1985)

[5] W.H. Butler: Phys.Rev. **B31**, 3260, (1985)

[6] J.O. Linde: Ann.Phys. **30**, 151, (1937)

[7] P.L. Rossiter: *The Electrical Resistivity of Metals and Alloys.* Cambridge University Press, Cambridge, 1987

[8] P. Weinberger: *Electron Scattering Theory for Ordered and Disordered Matter.* University Press, Oxford, 1990