

Optical Conductivity of Disordered Alloys Calculated from First Principles

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The optical conductivity of random Ag-Au alloys was calculated applying the KKR-CPA method and the Kubo-Greenwood equation. Drude's law was fitted to the calculated conductivity for low frequencies to allow for a discussion of the free electron model and to obtain optical relaxation times which could be compared to experimental data. The imaginary part of the dielectric function calculated from the conductivity was split into intraband and interband contributions and was also compared to measured data. Possible reasons for the obtained differences in the interband transition onset energy as well as extensions of the formalism to more complicated systems are discussed. [S0031-9007(99)08650-0]

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The optical properties of random alloys, especially of thin ferromagnetic films, play an important role in modern mass storage applications and are therefore attracting a lot of interest [1,2]. Unfortunately, until now it has not yet been possible to calculate these properties from first principles, i.e., in a completely parameter-free way. Such parameter-free calculations have been shown to be extremely useful for discussing real physical phenomena in complex metallic systems and also for taking a further step towards a computer-aided design of materials.

The Korringa-Kohn-Rostoker (KKR) method in conjunction with the coherent potential approximation (CPA) [3] and local density functional theory allows for an accurate numerical description of many physical properties of random alloys from first principles. dc transport coefficients have been calculated with great success for both paramagnetic [4,5] and ferromagnetic [6] alloys. Calculations of transport coefficients for optical frequencies, however, have been performed only in a simplified way for

rather crude tight-binding Hamiltonians [7,8] or for one-dimensional model alloys [9].

It is the purpose of the present paper to show how optical conductivities or, alternatively, the imaginary part of the dielectric function of random metallic systems can be calculated by combining a sophisticated multiple scattering approach to the electronic structure problem, the KKR-CPA, with the very general Kubo formula for solving the transport equation. As an application of the formalism, the real part of the optical conductivity of the disordered bulk alloy silver-gold is calculated using nothing but experimental lattice constants as an input. At the end of the paper, the generalization of the formalism to more complicated systems, namely, ferromagnetic or layered systems or systems with a surface, is outlined.

In linear response theory the real part of the conductivity of a disordered system at arbitrary frequencies ω is given in terms of the Kubo-Greenwood equation [10]:

$$\text{Re}[\sigma_{\mu\mu}(\omega)] = \frac{\pi}{V} \int d\epsilon \frac{f(\epsilon) - f(\epsilon + \hbar\omega)}{\omega} \text{Tr} \langle \delta(\epsilon - H) j_{\mu} \delta(\epsilon + \hbar\omega - H) j_{\mu} \rangle_{\text{conf}}, \quad (1)$$

where f , j , and V are the Fermi function, the electronic current operator, and the volume of the system, respectively. The brackets indicate that a configurational average over all configurations of the disordered alloy has to be taken. For the cubic systems considered in this paper, the three diagonal components of the tensor $\sigma_{\mu\mu}$ are equal and we therefore merely write σ_1 for their real part. At zero temperature one can write $\sigma_1(\omega)$ in terms of the Green function of the system:

$$\sigma_1(\omega) = \frac{1}{V\omega\pi} \int_{\epsilon_F - \hbar\omega}^{\epsilon_F} d\epsilon \times \text{Tr} \langle \text{Im} G(\epsilon) j_{\mu} \text{Im} G(\epsilon + \hbar\omega) j_{\mu} \rangle_{\text{conf}}. \quad (2)$$

For $\omega = 0$ this expression reduces to the usual dc expression which is given by

$$\sigma(0) = \frac{\hbar}{V\pi} \text{Tr} \langle \text{Im} G(\epsilon_F) j_{\mu} \text{Im} G(\epsilon_F) j_{\mu} \rangle_{\text{conf}}. \quad (3)$$

It is shown in Ref. [11] how this dc conductivity can be evaluated in the framework of the KKR-CPA by expressing the average over the product of Green functions in terms of configurationally averaged CPA single-site Green functions and approximately evaluating the so-called vertex corrections. Now Eq. (2) contains basically the same expressions as the dc expression [Eq. (3)] with the only difference that pairs of different energies occur in Eq. (2) and an additional energy integral has to be performed. One can therefore calculate the integrand of Eq. (2) by means of a modified version of the dc expressions given by Ref. [11]. Because in contrast to dc calculations one has a variety of photon energies and also has to carry out

an energy integration, calculations of the optical conductivity are very time consuming.

In order to demonstrate the new technique, the alloy system silver-gold was chosen. It has the advantage that for low photon energies the behavior of the electrons is expected to be free electronlike with interband transitions occurring only for photon energies above a certain threshold. One can therefore study the intraband and interband regimes separately. Moreover, quite some experimental data is available for Ag-Au. Note that the approach is not limited to such comparably simple alloys. Any alloy system can be treated with this combination of local density theory, KKR-CPA method, and the Kubo formalism no matter how strong electron scattering is.

For the calculation of the optical conductivity, self-consistent alloy potentials were generated in a first step by iterating the KKR-CPA equations until charge self-consistency was achieved [12]. Based on these potentials, the KKR-CPA equations were solved once more for a dense mesh of real energies covering the energy range occurring in the energy integration in Eq. (2). The angular momentum expansion was carried out up to $\ell = 2$. A scalar relativistic approach including all relativistic effects except spin-orbit interaction was chosen. Using the results of the KKR-CPA calculation, the optical conductivity was then evaluated for a number of photon energies between 0.01 and 2 Ry by means of Eq. (2). Moreover, for each alloy an additional dc calculation was performed using Eq. (3).

The result of one such calculation is shown in Fig. 1 for the alloy $\text{Ag}_{50}\text{Au}_{50}$. One sees that starting from $E = 0$ the conductivity drops quickly as the photon energy is raised. At about 2 eV a minimum is observed after which the conductivity begins to rise again. The position of the minimum is easily identified as the energy of the d -band

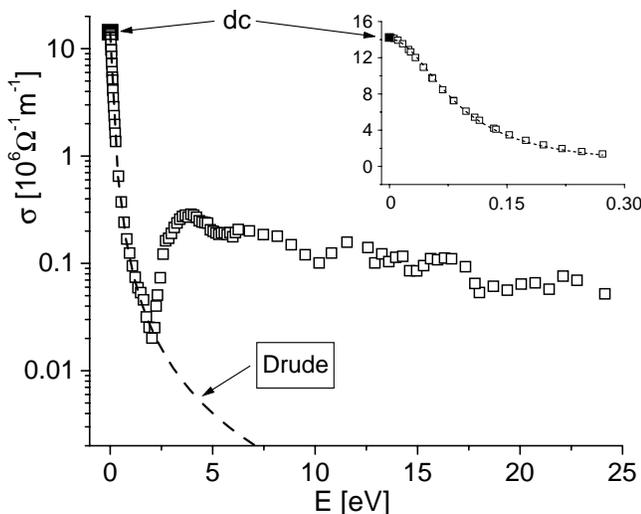


FIG. 1. Optical conductivity of a $\text{Ag}_{50}\text{Au}_{50}$ alloy. Open squares: calculated values for $\sigma(\omega)$; solid square: calculated dc value; broken line: Drude's law fitted to calculated data in the low-frequency regime below 2 eV (using $\tau = 7 \times 10^{-15}$ s). Inset: regime of very low photon energies.

complex with respect to the Fermi energy. Above this energy interband transitions between the conduction band and the lower lying d bands contribute to $\sigma(\omega)$.

Drude's theory for free electrons predicts a variation of $\sigma_1(\omega)$ of the following form:

$$\sigma_1^{(D)}(\omega) = \frac{\sigma(0)}{1 + (\omega\tau)^2}, \quad (4)$$

where τ is the relaxation time. This formula was fitted to the calculated $\sigma_1(\omega)$ for energies below the onset of interband transitions, where the electrons have mainly s and p character and behave similar to free electrons. The result of one such fit is shown in Fig. 1. One sees that for low frequencies the calculated $\sigma_1(\omega)$ indeed obeys Drude's law very well. Optical relaxation times τ obtained by means of this fitting procedure are displayed in Fig. 2 for all of the alloys together with some experimental values for τ . Obviously, the calculated relaxation times τ show the same concentration behavior as the measured ones, but their absolute values are higher. As the measured data were obtained at room temperature, an obvious source for this discrepancy is the thermal contribution to optical relaxation. One can use experimental residual resistivity ratios [14] to take account of this effect and obtain corrected experimental relaxation times corresponding to low temperatures (Fig. 2). The agreement between calculation and experiment is much better now, and the remaining difference can be attributed to effects of surface roughness or contaminations which are known to reduce significantly experimental optical relaxation times [15].

In Fig. 2 the relaxation time τ is also compared to the calculated dc conductivity. One sees that $\sigma(0)$ is almost perfectly proportional to τ as one, of course, expects from Drude's formula for the dc electrical conductivity, $\sigma(0) = ne^2\tau/m^*$, where n is the density of electronic carriers, and m^* is the reduced mass. Using the free

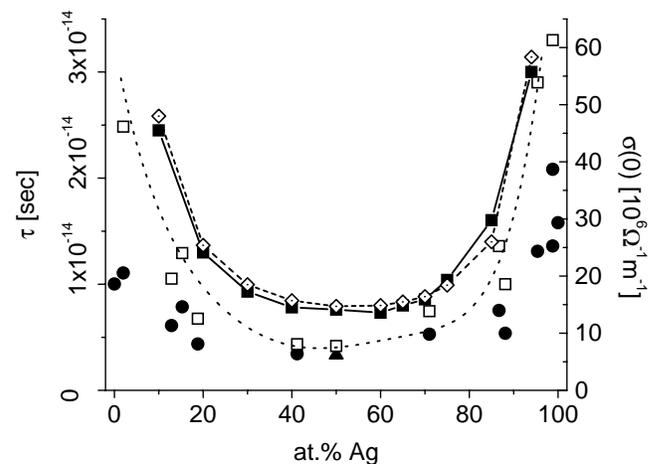


FIG. 2. Relaxation time τ and dc conductivity $\sigma(0)$ of Ag-Au alloys. Solid squares: calculated values for τ obtained by fitting Drude's law to the calculated $\sigma(\omega)$; solid triangle [8] and solid circles [13]: experimental values for τ ; open squares: experimental values corrected for thermal relaxation processes (dotted guideline); diamonds: calculated dc conductivity

electron density n_{free} which is $5.86(5.90) \times 10^{28} \text{ m}^{-3}$ for Ag(Au), assuming one conduction electron per atom, and reading the proportionality factor $\sigma(0)/\tau = ne^2/m^*$ from Fig. 2, one obtains $(n/m^*) \approx 1.2 \times (n_{\text{free}}/m_{\text{free}})$, where m_{free} is the free electron mass. For one electron per atom, i.e., $n = n_{\text{free}}$, the reduced mass is therefore about 0.8 times the free electron mass for all of the Ag-Au alloys. This result agrees with experimental findings [13].

From σ_1 the imaginary part of the dielectric function ϵ_2 can be calculated. One can split ϵ_2 into a part corresponding to Drude-like intraband (D) and interband contributions (i):

$$\epsilon_2(\omega) = \frac{\sigma_1}{\epsilon_0 \omega} = \epsilon_2^{(D)}(\omega) + \epsilon_2^{(i)}(\omega), \quad (5)$$

where ϵ_0 is the vacuum permittivity. The interband contribution $\epsilon_2^{(i)}(\omega)$ was calculated by subtracting from the total $\epsilon_2(\omega)$ the intraband contribution $\epsilon_2^{(D)} = \sigma_1^{(D)}(\omega)/\epsilon_0 \omega$ given by Eq. (4) using the relaxation times τ shown in Fig. 2. Some of the results for $\epsilon_2^{(i)}$ are shown in Fig. 3 together with experimental data. One sees that both experimental and theoretical curves show a similar behavior: $\epsilon_2^{(i)}$ is zero for energies below a certain energy $E^{(i)}$ —the onset of interband transitions—and reaches a maximum at an energy $E_{\epsilon_{\text{max}}}$ which is 1.5 to 2 eV above this onset energy. For even higher energies $\epsilon_2^{(i)}$ decreases again. There is a very good agreement between experiment and calculations concerning the absolute value of $\epsilon_2^{(i)}$ especially for gold-rich alloys. Even the shoulder occurring for the low silver alloy (20%) at about 2.8 eV is well reproduced by the calculations. A certain disagreement, however, is found for the energies where interband transitions start ($E^{(i)}$) and where the maximum of $\epsilon_2^{(i)}$ is located ($E_{\epsilon_{\text{max}}}$). To make this clear, $E^{(i)}$ and $E_{\epsilon_{\text{max}}}$ are shown in Fig. 4 as a function of alloy composition. The calculated onset energies and maximum positions are indeed lower than the corre-

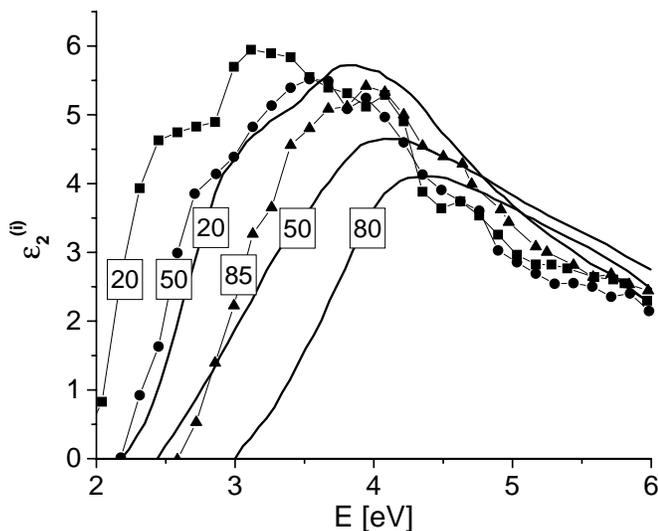


FIG. 3. Interband contribution to ϵ_2 of Ag-Au alloys. Lines with solid symbols: calculated values; other lines: experimental values [16]. The curves are labeled with the Ag concentration.

sponding measured ones by 0.3 to 1 eV depending on the experimental source and on the alloy composition. There are several possible explanations for the observed discrepancies which were also observed by other authors, e.g., for pure Ag, where a calculated $E^{(i)}$ was found to be 0.6 eV too low [18]. First of all, the calculations presented here are based on perfect infinite bulk systems, whereas the measurements might be influenced by the surfaces where the electronic structure differs from the electronic structure in the bulk and where the lattice is distorted in the uppermost layers. Moreover, the surface might be rough or be covered with adsorbates of all kinds. Also, the films prepared for optical measurements usually contain large amounts of stresses leading to an additional variation of the lattice constant [15]. Comparing the experimental results for $E^{(i)}$ given by various sources (see Fig. 4), one sees that there is quite some uncertainty, probably due to some of the effects mentioned.

As calculations of the optical conductivity of alloy surfaces or films are not feasible at the moment in the same rigorous parameter-free way as for bulk alloys, these possible reasons are difficult to verify. However, one can try to estimate $E^{(i)}$ from the density of states (DOS). The onset energy should be roughly the distance between the Fermi energy and the d -band complex. For pure gold, the electronic structure of a semi-infinite system with a surface has been calculated using the screened KKR method [19], and the DOS was given for various planes parallel to the surface. It seems that the d -band complex is indeed somewhat closer to the Fermi energy for the

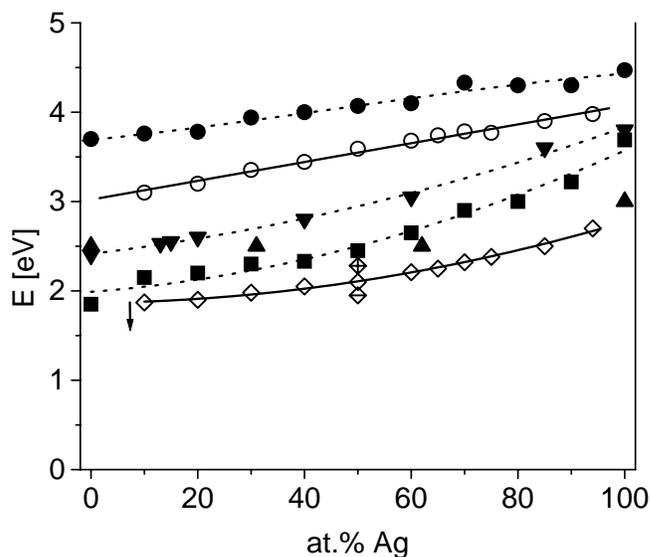


FIG. 4. Onset energy of interband transitions $E^{(i)}$ and energy $E_{\epsilon_{\text{max}}}$ where $\epsilon_2^{(i)}$ has its maximum. Empty diamonds: calculated $E^{(i)}$ based on experimental lattice constants; diamonds with symbols: results for modified lattice constants ($\pm 1.5\%$); empty circles: calculated $E_{\epsilon_{\text{max}}}$. Full symbols: experimental values for $E^{(i)}$ (down triangles [13], squares [16], up triangles [17]) and $E_{\epsilon_{\text{max}}}$ (full circles [16]). Arrow: estimated correction for the onset energy in gold-rich alloys due to an inclusion of spin-orbit effects in the calculations.

uppermost surface layer than for the deeper lying layers, but the shift in energy is definitely below 0.3 eV.

In order to estimate the effect of a varying lattice constant, two sets of calculations were carried out for the alloy Ag₅₀Au₅₀ using artificial lattice constants which were 1.5% higher and lower than the true experimental lattice constant used in the calculations already described. One finds that the higher lattice constant leads to a 0.2 eV increase of $E^{(i)}$, whereas the lower lattice constant leads to a corresponding reduction. Thus, the two surface effects discussed so far could sum up to 0.5 eV and at least partially explain the observed energy shifts of $E^{(i)}$.

A further possible explanation for the shifts has to do with the foundation of the electronic structure theory used here: The underlying local density functional theory is valid only for the electronic ground state and might fail for the excited states occurring when interband transitions take place. This was suspected by some authors, e.g., in Ref. [18]. As local density functional theory is often successfully used even for excited states, we think that some shortcomings of density functional or local density theory should not be the only reason for the quite pronounced discrepancies observed.

All calculations were carried out scalar relativistically, i.e., neglecting spin-orbit interactions. A fully relativistic treatment would not change the d -band position but only increase its width (for gold by up to 0.7 eV) and therefore further reduce the separation between the d band and the Fermi energy by up to 0.35 eV (arrow in Fig. 4). The omission of spin-orbit effects can therefore not be the explanation for the observed deviations, but their inclusion would partially explain the difference in the size of these deviations between silver- and gold-rich alloys because for silver-rich alloys the effect is smaller.

The coherent potential approximation neglects all forms of short-range order which might occur in an alloy. Short-range order effects are known to change residual dc resistivities by up to 10% in some cases and also have an influence on optical properties [20]. However, the system Ag-Au is not known to show short-range order so that this explanation has to be ruled out also.

Future extensions of the theory, e.g., to magneto-optical conductivities of certain alloys, promise an analogous parameter-free approach to these technologically extremely important systems. Magneto-optical calculations can be carried out only for translationally invariant systems or systems with single impurities until now (e.g., Ref. [21]) and not for random alloys. For bulk random systems, an extension seems realistic for the near future because a relativistic description for dc transport coefficients of ferromagnets is already available [6]. A relativistic treatment makes it easy to deal with effects which arise from spin-orbit coupling such as the magneto-optical effects [2] already mentioned. One merely has to evaluate Eq. (2) using the relativistic CPA Green function to obtain symmetry-reduced optical conductivity tensors.

An extension of the formalism to layered systems is also realistic. The screened KKR-CPA method has been successfully applied to the calculation of dc conductivities of multilayer systems recently [22]. A generalization to optical conductivities is straightforward following the concepts of the present paper but requires extensive computational resources.

In summary, the first principles theory presented here yielded the first rigorous parameter-free calculation of frequency dependent transport quantities for disordered alloys. This is a major step towards a parameter-free description of electronic transport in any type of disordered metallic system. An impressive agreement between calculated and measured dielectric functions was achieved. The remaining differences are probably caused by changes of the electronic structure and the lattice constant near the surface which are not included in the calculations. The method presented should be extendable to magnetic or layered systems in a straightforward way.

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