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Frequency dependence of the Drude relaxation time in metal films: Further evidence for a two-carrier model*

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We examine optical and energy-loss data on a variety of metals in light of a recently proposed two-carrier model of metallic optical conductivity in which the two carriers are electrons located in crystallites and in grain boundaries, respectively. We find that many of the published measurements of optical properties of metals appear to be strongly influenced by sample crystallinity and that these measurements support this simple model.

In a recent paper[1] we concentrated almost entirely on showing how a simple two-carrier model was able to fit the infrared dielectric response of gold films, in particular, explaining an observed frequency dependence of the Drude relaxation time τ. In the present paper we will examine additional evidence obtained from optical and electron-energy-loss experiments which tend to support that theory. We will show that this model is applicable to a variety of results by demonstrating how it can be used to explain puzzling anomalies, not only in other materials besides gold, but also in other regions of the frequency spectrum besides the infrared. Furthermore, we will show that this model displays the same temperature dependence as the data in one case.

The model is based on having two different types of current carriers in the metal: carrier (a) comes from inside crystallites (where τ_a is large), while carrier (b) comes from within grain boundaries (where τ_b is very short). From this assumption, the apparent collision frequency, $(1/\tau)_{\text{eff}} = \omega\epsilon_2/(1-\epsilon_1)$, can be derived and shown to have a quadratic frequency dependence in a limited region. It is clear that this model is not necessarily limited to any particular type of metal since it only depends on having a sufficient amount of disorder in the sample.

In Ref. 1 we have already mentioned that the anomalous absorption seen in aluminum deposited on cold substrates[2] could be understood in terms of this model. Inelastic-electron-scattering experiments have also shown a dependence on sample crystallinity in aluminum. Kunz[3] and later Von Festenberg[4] measured both the width of the Al 15-eV plasma resonance line and the mean crystallite size in a series of samples. They found the linewidth decreased as the samples were annealed. Subsequently, Krishan and Ritchie[5] carried out a calculation using perturbation theory of the contribution to the width of elastic scattering of the plasmon by density inhomogeneities. They found that measurements of the plasmon width as a function of momentum transfer provide a direct measure of the autocorrelation function of the density inhomogeneities. This bears directly on our model. Suppose the density variations are random. Then the range of the autocorrelation function and the mean crystallite size as determined by electron diffraction should agree. If, on the other hand, the important density variations are due to grain boundaries, the situation is different. Since adjacent grains may be roughly the same size, the range of the autocorrelation function should be larger than the mean crystallite size. If all the crystallites were exactly the same size and had the same orientation, this range would be infinte.

Krishan and Ritchie used a Gaussian autocorrelation function and adjusted its range to fit Von Festenberg's data. The resulting range was 210 Å in a sample for which the mean crystallite size was 70 Å. This result is consistent with our model and suggests a coherence length for crystallite size of about three times the average crystallite size. In other words, a given crystallite and its adjacent neighbors tend to be about the same size.

In Ref. 1 we argued that the variation in relaxation time in grain boundaries, not the density, dominates in scattering *electrons*. Krishan and Ritchie assumed the converse is true when *plasmons* scatter from grain boundaries. Whether these two approaches are in violent opposition, whether they represent independent choices, or whether the correct choice may depend on the details of grain-boundary formation is unclear to us at present. We wish to point out that we can obtain the correct order of magnitude for the increased plasmon width at small q by including only the increased value of $\epsilon_2(\omega_p)$ due to relaxation-time effects. For example, Kunz found a plasmon width of 4, 3, and 1.5 eV for crystallite sizes of 25, 60, and 230 Å, respectively. Using values of τ_a and τ_b

which are the same as those used to fit the aluminum data of Ref. 2, and assuming that the disordered regions extend three monolayers into each grain, we find disorder contributions to the width of 2.8, 1.9, and 0.74 eV, respectively. Assuming an intrinsic width plus experimental resolution of 0.9 eV, these results are seen to be in fair agreement with the measured values. Therefore, it appears that at this time the dominant mechanism of plasmon scattering in disordered metals is uncertain: It could be either variations in density or variations in mean-free time due to grain boundaries. That the extra width as a function of momentum transfer gives a measure of the autocorrelation function of the disorder would seem to hold in either case.

We have also examined data on the alkali metals. In Figs. 1 and 2 the infrared data of Smith[6] on sodium and potassium is shown along with the predictions of this model. For sodium the parameters used in Eq. (4) of Ref. 1 are $1/\tau_a = 0.325\times 10^{14}$ sec^{-1}, $\tau_b = 0.015\times 10^{-14}$ sec, and $B/A = 0.05$. For potassium $1/\tau_a = 0.25\times{}^{14}$ sec^{-1}, $\tau_b = 0.03\times 10^{-14}$ sec, and $B/A = 0.02$. The value for B/A is essentially given by the ratio of the total number of electrons existing in the grain boundaries to the total number of electrons existing in the crystallites themselves. The physical meaning of these parameters is given in more detail in Ref. 1. In these figures we have not used any sophisticated curve fitting. As in Ref. 1, the value of τ_a is determined by the low-energy part of the spectrum and is perhaps the most reliable of the three numbers. The other two, τ_b and B/A, both contribute to the frequency dependence. The values are chosen such that the curvature of the graph is correct: This is determined primarily by the value of τ_b. As a rough estimate, therefore, we expect that our three parameters are accurate to within 5% for $1/\tau_a$ and to within 10% for τ_b and B/A. [However the product, $(B/A)\tau_b$, is less questionable and should be accurate to within 5%.]

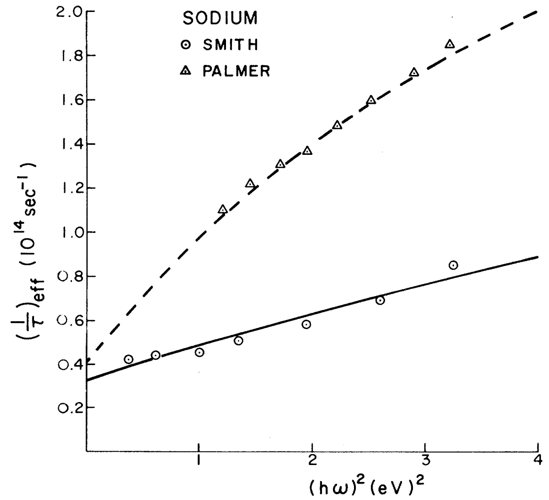

FIG. 1. $(1/\tau)_{\rm eff}$ vs $(\hbar\omega)^2$ for sodium. Data are taken from Ref. 6 (⊙) and from Ref. 9 (△). The parameters used in the two-carrier fit are given in the text.

Two other explanations have been advanced for this behavior in the alkali metals.[7,8] Neither of these is consistent with the large variation of the frequency dependence seen on different samples of the same material. For example, note the difference in Fig. 1 between Smith's data on sodium and that of Palmer[9] on the same material. Our model can fit this additional data as well. In Fig. 1 the dashed line shows the predicted relaxation time with the parameters $1/\tau_a = 0.4\times 10^{14}$ sec^{-1}, $\tau_b = 0.025\times 10^{-14}$ sec, and $B/A = 0.115$. Note that this gives a value of the bulk collision frequency close to that of Smith, as would be expected. The value of τ_b used to fit the sodium data may seem too small to be physically reasonable. Part of the increase in $(1/\tau)_{\rm eff}$ may indeed be arising from other effects, such as described in Refs. 1, 7, and 8. However, the fact that the relaxation time is sample dependent strongly indicates that the effects explained by our model contribute a large part to the behavior, and is responsible for the bulk of the frequency dependence found by Palmer. That these two measurements on the same material should give different results is reasonable since the method of sample preparation was different in the two cases. Smith evaporated his samples slowly onto a room-temperature quartz bar and measured the optical properties of the quartz-metal interface. Palmer evaporated his samples rapidly onto a nitrogen temperature sapphire substrate, annealed them at room temperature, and measured the optical properties of the vacuum-metal interface. It is understandable that Palmer's samples might have more residual-bulk disorder than

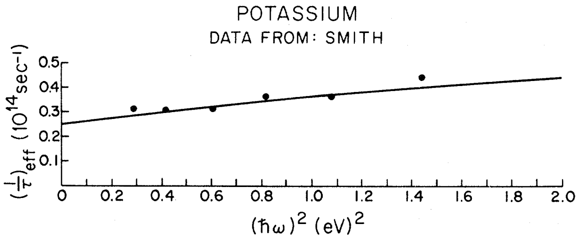

FIG. 2. $(1/\tau)_{\rm eff}$ vs $(\hbar\omega)^2$ for potassium. Data are taken from Ref. 6. The parameters used in the two-carrier fit are given in the text.

Smith's.

In regards to the value of τ_b it should also be emphasized that relaxation times as small as those used here have been seen in many liquid metals. In tin and lead it was found[10] that the relaxation times could be as small as 0.035×10^{-14} sec and 0.022×10^{-14} sec, respectively. In indium and bismuth relaxation times of 0.062×10^{-14} sec and 0.015×10^{-14} sec were found.[11] Such small relaxation times should therefore not be surprising for the amorphous region of the grain boundary. It is possible, indeed, to expect values for the mean-free path that are smaller than the nearest-neighbor distance.[12] For the case of aluminum where the relaxation time measured in the liquid[13] is significantly larger than the one we have assumed, the discrepancy may be due to the grain boundaries being even more inhomogeneous than the liquid, containing, as it probably does, larger density fluctuations. The scattering potential for the atoms in the grain boundaries where large voids may exist can thus be greater than for those in the liquid. This is substantiated by measurements of the resistivity in grain boundaries of aluminum and copper[14] which indicate that these regions are much more disordered than the liquid.[12]

We have indicated that, as in the case of the aluminum plasmon discussed above, this two-carrier model could be important in the interpretation of the ultraviolet optical properties of metals having a large amount of disorder. In a recent paper on indium,[15] considerable absorption was found at high energies, up to 10 eV, that the authors could not attribute to interband transitions calculated from their band structure. We suggest that this absorption could also be due to free-carrier absorption. In Fig. 3 we show the quantity $(1/\tau)_{\text{eff}} = \omega\epsilon_2/(1-\epsilon_1)$ taken from their data along with the prediction of our model with $1/\tau_a = 2.0 \times 10^{14}$ sec^{-1}, $\tau_b = 0.014 \times 10^{-14}$ sec, and $B/A = 0.45$. Effects due to band structure have not been included so that the predicted curve should always lie below the data. The peaks in the data at 2 and 6 eV are due to interband transitions. It is not surprising that indium can have such a high-volume fraction of disordered material at room temperature. It has been shown[16] that even when cooled from the melt to room temperature, indium can be almost totally amorphous.

The infrared optical constants of indium have also been measured at various temperatures.[17] These data again show the characteristic frequency variation of the relaxation time. According to the model, the temperature dependence of this effect can be calculated. (This is true only when it can be assumed that no change in sample crystallinity takes place upon varying the temperature, e.g., annealing of the sample at higher temperatures or severely straining it at lower temperatures.) Both τ_b and B/A should be temperature independent, and only $1/\tau_a$ should vary. Its variation can be predicted on the normal manner, following Holstein[18]:

$$\frac{1}{\tau}(0°) = \frac{2}{5}\,\frac{\Theta_D}{T}\,\frac{1}{\tau}(T)\,. \tag{3.6}$$

We have used the handbook value of the Debye temperature, $\Theta_D = 106$ K.[19] The results of these calculations are shown in Fig. 4. The parameters used are $B/A = 0.8$, $\tau_b = 0.03 \times 10^{-14}$ sec, and $1/\tau = 2.05 \times 10^{14}$ sec^{-1}, at 295 K. We see that the result of measurements at one temperature can be predicted from measurements at another temperature with no additional parameters.

We have collected considerable supporting evidence for the validity of the two-carrier model based on partial-sample disorder. This has included data on several different materials. The

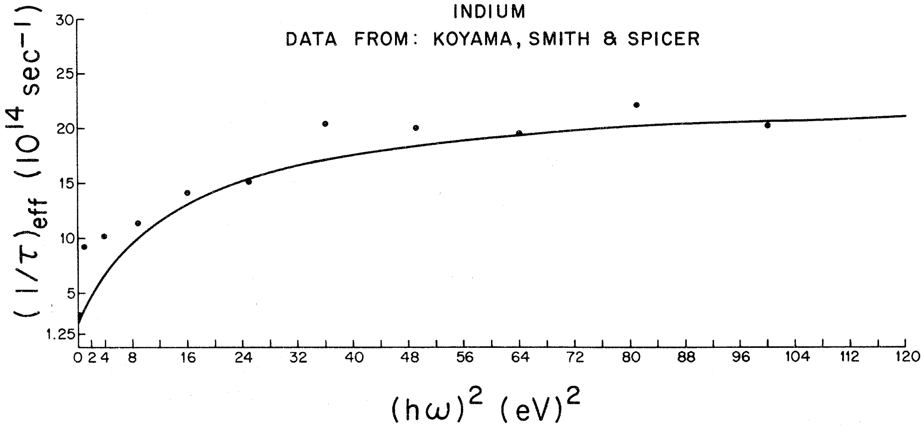

FIG. 3. $(1/\tau)_{\text{eff}}$ vs $(\hbar\omega)^2$ for indium. Data are taken from Ref. 13. The parameters used in the two-carrier fit are given in the text.

data on sodium and aluminum, as well as that previously presented on gold, demonstrates that the frequency variation of the Drude relaxation time is strongly dependent on the preparation of the sample: The more disordered the sample, the greater will be the frequency variation. The data on indium also indicates that the temperature dependence predicted by our model is in agreement with experiment.

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Note added in proof. We would also like to point out the applicability of this model to the optical properties of alloys. Recently, Flaten and Stern[20] found that for AgSn alloys, a term $\sigma_D/\hbar\omega$ must be added to the Drude ϵ_2 for which no theoretical justification was given, an assumption which is equivalent to attributing a quadratic frequency dependence to the collision rate. We would expect that the two-carrier model would be capable of explaining these results if the sample was not homogeneous, i.e., with the Sn preferentially concentrated along grain boundaries preventing any self-annealing.

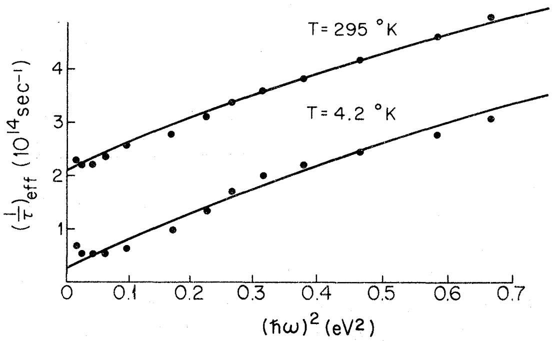

FIG. 4. $(1/\tau)_{\mathrm{eff}}$ vs $(\hbar\omega)^2$ for indium in the infrared at two temperatures. The data are taken from Ref. 15. The parameters used in the two-carrier fit are given in the text.

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