PHYSICAL REVIEW B VOLUME 24, NUMBER 2 15 JULY 1981

Brief Reports

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Single-particle — collective-mode coupling and the Mie resonance in small metallic particles: Optical properties of colloidal Na in NaCl

R. P. Devaty and A. J. Sievers

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

An absorption mechanism based on coupling between the conduction electrons and the collective Mie resonance is proposed to explain the optical properties of small Na particles.

The characteristic feature of the optical absorption spectrum of a system containing dispersed ultrafine metallic particles (diameter ≤ 100 Å) is the sphere resonance, which was first explained by Mie.[1] The resonance has been thoroughly investigated experimentally.[2] Although the Mie theory corrected for boundary scattering provides approximate agreement with the data, a systematic red shift of the peak position and asymmetry of the line shape observed for particles of the "simple metals" remain unexplained. Granqvist and Hunderi[3] found agreement between transmission data on evaporated Au particles and a model which includes optical data on bulk Au only after the introduction of a fictitious plasma frequency which is lower than for bulk Au. Red shifts are also observed for alkali-metal colloids embedded in alkali-halide matrices.[2] These systems are favorable for comparison with theoretical models because the optical properties of bulk alkali metals are relatively well understood and the alkali halides are transparent to electromagnetic radiation within the frequency range of interest.

Perhaps the optimal model system is NaCl:Na because the equilibrium betwen F centers and colloids is most favorably weighted towards colloids.[4] Smithard and Tran[5] measured the dependence of the wavelength for maximum absorption on particle size for this sytem and compared the results with a Drude-plus-interband model that included Smith's[6] optical data on Na films. The theory predicts little size dependence of the peak position for the smallest particles, in disagreement with the data, which show an increasing red shift of the peak with decreasing particle size.

The role of interband transitions with regard to the red shift of the peak is an important question. The optical properties of bulk Na (Ref. 6) display a feature in the same frequency region as the Mie resonance which has long been attributed to interband transitions. However, a detailed examination[7] of the interband model yields a maximum possible optical mass enhancement of a few percent, which is insufficient to explain either Smith's data or the red shift. A recent analysis[7,8] based upon coupling between the conduction electrons and surface plasmons and which ignores interband transitions provides improved agreement with the bulk data. Also, the existence of interband transitions in small particles is called into question by optical data on microcrystalline Al films,[9] which show that the interband contribution vanishes for grains smaller than about 50 Å.

In this article, we reexamine the optical properties of small metallic particles. We present a phenomenological model based on a single new parameter, which represents coupling between the quasiparticles and the collective dipole resonance, to resolve the discrepancy between theory and experiment. In particular, we apply the model to the data of Doyle[4,10] on colloidal Na in NaCl. Interband transitions are completely ignored in this treatment.

The standard theory for optical absorption by a composite medium of small metallic particles in a dielectric host treats the conduction electrons within the Drude model. The parameters are the plasma frequency ω_p, the relaxation time τ, and the high-frequency dielectric constant including core polarizability ϵ_∞. The contribution of interband transitions can also be included, if desired. To account for the width of the resonance, the relaxation time must be modified to include scattering of the conduction electrons by the surface of the particle.[4,11] If the bulk and surface processes are independent and the surface scattering is isotropic, then

$$1/\tau = 1/\tau_b + v_F/R \ , \tag{1}$$

where τ_b is the relaxation time of the bulk metal, v_F is the Fermi velocity, and R is the particle radius. In the limit of small metal volume filling fraction f, the absorption coefficient is

$$\alpha(\tilde{\nu}) = 18\pi f \epsilon_0^{3/2} \tilde{\nu} \epsilon_2 / [(\epsilon_1 + 2\epsilon_0)^2 + \epsilon_2^2] \ , \tag{2}$$

which is the Mie[1] result for the limit of small particle size. Here, $\epsilon(\omega) = \epsilon_1 + i\epsilon_2$ is the dielectric function of the metal and ϵ_0 is the dielectric constant of the host medium. For $\omega_p \tau >> 1$, the resonance frequency is

$$\omega_0 \cong \omega_p / (2\epsilon_0 + \epsilon_\infty)^{1/2} \tag{3}$$

and the linewidth is determined by ϵ_2.

The introduction of coupling between the conduction electrons and the collective resonance as an additional channel for electronic relaxation is motivated by a successful application of coupling between the conduction electrons and surface plasmons to explain a feature in the optical properties of bulk Na, K, and Rb.[7,8] Surface plasmons and the sphere resonance are related phenomena. The coupling should be greater in a small particle due to the large surface-to-volume ratio.

An interaction Hamiltonian between the collective resonance and conduction electrons can be written down by analogy with the electron-surface plasmon problem once the vector potential of the sphere resonance is known. The contribution to the optical conductivity of the second-order process of photon absorption and simultaneous creation of a collective oscillation and an electron-hole pair is calculated in the weak coupling limit. The contribution to the electronic relaxation time at zero temperature is[12]

$$\frac{1}{\tau_i(\omega)} = \frac{2\pi}{\omega} \int_0^\omega d\omega' (\omega - \omega') \alpha^2 F(\omega') \ , \tag{4}$$

where $\alpha^2 F(\omega)$ is the sphere-mode density of states times a coupling constant. As a simplification, we approximate $\alpha^2 F(\omega)$ by a delta function at the sphere resonance frequency. Thus

$$\alpha^2 F(\omega) \cong \tfrac{1}{2} \lambda(0) \omega_0 \delta(\omega - \omega_0) \ , \tag{5}$$

where $\lambda(0)$ is an effective coupling constant. We have ignored the linewidth of the resonance. With this ansatz, Eq. (4) becomes

$$\frac{1}{\tau_i(\omega)} = \begin{cases} 0, & \omega < \omega_0 \\ \pi\lambda(0)\omega_0(1 - \omega_0/\omega), & \omega > \omega_0 \ . \end{cases} \tag{6}$$

The gradual turn-on of the relaxation time is a consequence of phase-space restrictions imposed by energy conservation. The corresponding mass enhancement $\lambda(\omega)$, defined by

$$\lambda(\omega) = m(\omega)/m - 1 \ , \tag{7}$$

where m is the bare electron optical mass and $m(\omega)$ is the effective mass, is[12]

$$\lambda(\omega) = \lambda(0) \frac{\omega_0}{\omega} \left[\frac{\omega_0}{\omega} \ln \left| \frac{\omega^2 - \omega_0^2}{\omega_0^2} \right| - \ln \left| \frac{\omega - \omega_0}{\omega + \omega_0} \right| \right] \tag{8}$$

The frequency dependence of $1/\omega\tau_i(\omega)$ and $\lambda(\omega)$ is displayed in Fig. 1. The modifications to the Drude parameters are

$$\omega_p^2(\omega) = \omega_p^2 / [1 + \lambda(\omega)] \ ,$$
$$1/\tau(\omega) = [1/\tau_b + v_F/R + 1/\tau_i(\omega)] / [1 + \lambda(\omega)] \ . \tag{9}$$

The mass enhancement alters all three contributions to the relaxation time because it modifies the band-structure effective mass. Equation (9) is used with Eq. (2) to obtain an absorption coefficient which can be compared with experiment. The approximate resonance frequency becomes

$$\omega_0 \cong \omega_p / \{(2\epsilon_0 + \epsilon_\infty)[1 + \lambda(0)\ln 4]\}^{1/2} \ . \tag{10}$$

Thus interaction between the quasiparticles and the collective resonance leads to a red shift of the frequency of maximum absorption.

The physical constants of Na used to compute

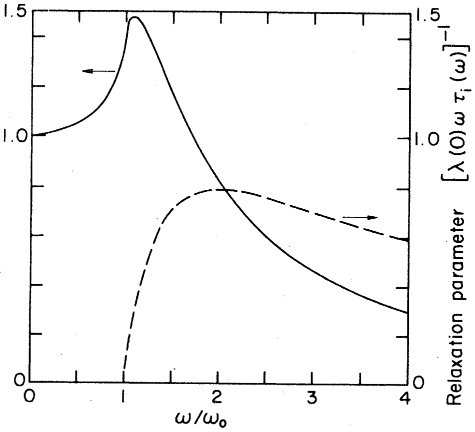

FIG. 1. Universal plot showing the frequency dependence of the mass parameter (solid line) and relaxation parameter (dashed line) obtained when a delta function is substituted for $\alpha^2 F(\omega)$ in the weak-coupling theory of Ref. 12.

the absorption coefficient were taken from Table I of Ref. 7. The dielectric constant of NaCl was taken to be $\epsilon_0 = 2.37$, which is valid near the resonance. The frequency dependence of ϵ_0 was ignored. The effective coupling constant $\lambda(0)$ was adjusted to fit the experimentally determined peak position. In the absence of a value for the volume filling factor, both the experimental and theoretical absorption curves were normalized to unity at the peak. The data do not include independent (nonoptical) information on the particle size or the distribution of sizes. Therefore we assumed spherical particles of uniform size. The particle size, which only appears in the size correction to the lifetime, was adjusted to match the full width at half maximum (FWHM) of the resonance. Clearly, optical data with associated particle size measurements would provide a more stringent test of the model.

Figure 2 shows our fits to three of Doyle's[4,10] experimental curves. Figure 2(a) also shows the prediction of the theory with the coupling constant set to zero, but no other parameters changed. Figure 2(b) shows an absorption spectrum for the same sample as Fig. 2(a) after a high-temperature heat treatment, which is thought to increase the size of the particles. Not only can the peak position be matched accurately, but the shape of the theoretical curves is asymmetric with a high-frequency tail, in agreement with experiment. Although the standard theory predicts some asymmetry, the coupling model introduces further absorption on the high-frequency side of the resonance. Since oscillator strength is pushed to higher frequencies, the additional relaxation mechanism actually leads to a decrease in the FWHM of the resonance. This effect can lead to errors in measurements of particle size on the basis of linewidth. Inclusion of the frequency dependence of the dielectric constant of NaCl pushes the wings of the resonance back slightly towards the peak.

The values of the coupling constant $\lambda(0)$ obtained from the fit range from 0.13 to 0.175. The effective coupling constant for electron-surface plasmon coupling in bulk Na is about 0.13,[7] so we find an enhancement of the coupling for small particles, as expected. Application of Eq. (10) to other systems of colloidal metal in alkali halides, e.g., the data tabulated by Doremus,[13] yielded $\lambda(0)$'s ranging from 0.08 to 0.30.

The data presented in Figs. 2(a) and 2(b) can be interpreted to imply an increasing red shift with decreasing particle size, although no independent size determination is available. Doyle's data are in agreement with the data of Smithard and Tran,[5] which display a red shift beyond that which can be obtained using the measured optical data for bulk Na.[6] The sphere-mode coupling model has no size dependence built into it beyond the surface scattering contribution to the electron lifetime. Particle size does not enter into Eq. (10), except indirectly through whatever dependence the phenomenological coupling constant might have on size. However, an increasing red shift with decreasing particle size

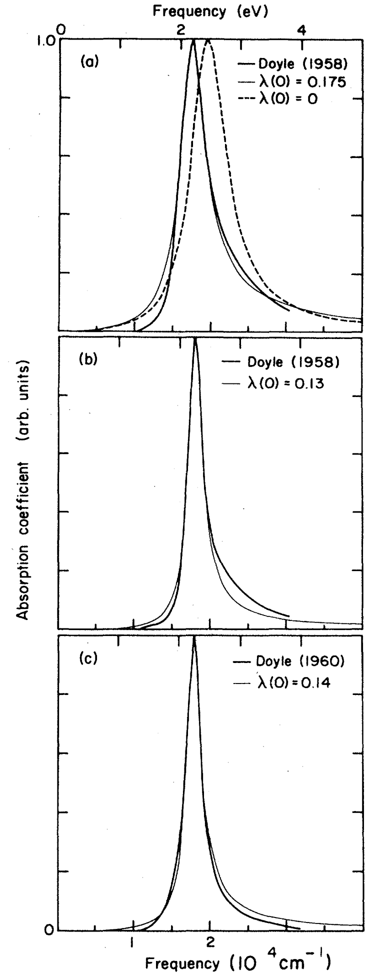

FIG. 2. Normalized optical absorption of colloidal Na. The curves are identified in the figure. The physical constants of Na used were taken from Ref. 7: $\omega_p = 5.91$ eV, $\tau_b = 2.94 \times 10^{-14}$ sec, $v_F = 1.053 \times 10^8$ cm/sec, and $\epsilon_\infty = 1.06$. For NaCl, $\epsilon_0 = 2.37$. The fitting procedure is described in the text. (a) The best fit was obtained for the particle diameter $x = 20$ Å. (b) The data are from the same sample as (a), but after a high-temperature heat treatment. Here $x = 40.5$ Å. (c) $x = 38$ Å.

agrees with the intuitive notion of increasing coupling with decreasing size due to reduced screening near the surface. A study of the size dependence of $\lambda(0)$ should yield information about the nature of screening and the electron-electron interaction in small systems.

The model provides agreement with the experimental peak position at the cost of an additional adjustable parameter. The predictive ability of the model resides in the details of the line shape. The model predicts that oscillator strength is pushed into the high-frequency tail. The peak is reduced in both height and width. Thus accurate measurments of the line shape performed with well-characterized samples are required to rigorously test the model.

One possible cause of the high-frequency tail is residual *F* centers. The absorption band for *F* centers in colored alkali halides is at higher frequencies than the colloid band. We chose NaCl:Na because of the favorable equilibrium of colloids with respect to *F* centers after heat treatment. The contribution of residual *F* centers to the absorption spectra in Fig. 2 is probably negligible.[14] In other systems of colloidal metal in alkali halides, residual *F* centers make an important contribution to the absorption which cannot be eliminated, so a detailed application of our model is difficult.

In summary, we have presented a phenomenological model based on coupling between the quasiparticles and the sphere mode in a small metal particle which can account for the anomalous red shift of the resonance. We obtained improved agreement between theory and optical data for a model experimental system, colloidal Na in NaCl. Further refinements in the model and experiments on well-characterized particles should lead to an improved understanding of electrons in confined systems.

We acknowledge helpful conversations with W. T. Doyle and D. M. Trotter. This work has been supported by NSF Grant No. DMR-76-81083 to the Cornell Materials Science Center, and by ARO Grant No DAAG-29-79-C-0170. Additional support was received from SERI Grant No DE-FG02-80C583113.

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