

Theory of far-infrared absorption by small metallic particles

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Strong infrared absorption by small metallic particles is shown to arise from the direct excitation of phonon modes by the field acting on unscreened surface ions. Absorption studies should provide a good source of information about the phonon density of states in small particles.

Recent experiments^{1,2} studied the far-infrared absorption by small metallic particles in an effort to observe structure due to quantization of conduction-electron energy levels predicted by Gorkov and Eliashberg³ (GE). Although the structure was not observed, the authors of Ref. 1 were able to explain its absence by noting that the particle diameters were not sufficiently uniform to permit the structure to be resolved. They were unable, however, to explain the size of the observed absorption. The absorptivity was over three orders of magnitude larger than that predicted by either GE or by a classical Drude theory including eddy-current losses. In this paper we propose an additional mechanism which appears to have been overlooked as a primary source of infrared absorption by small isolated particles, though it gives rise to much stronger absorption than found with the aforementioned theories.

In bulk metals an electric field is screened from the interior by the conduction electrons and there is little direct coupling between field and ions. Direct energy absorption by phonons requires a nonlocal relation between electron current and field and also that the electron mean free path be longer than the penetration depth of the field, so that the screening is not complete.⁴ In spite of these limitations the conversion of electromagnetic energy into acoustic energy is a well-known phenomenon.⁵⁻⁷ The experiments reported in Refs. 1 and 2 were performed on roughly spherical particles with diameters between 50 and 500 Å. For such particles the surface excitation region plays a more important role than in bulk samples. Near the surface the field is not screened⁸ and it can couple strongly to the surface ions. In addition the density of states for lattice vibrations is greatest in the infrared region. If the surface ions are driven at infrared frequencies which lie within the continuum of lattice eigenmodes, then bulk phonon modes can be excited. These modes are damped by the electron-phonon interaction, but it is the phonons which are directly excited by the field. Using reasonable choices of parameters, we will show that substantial absorption can re-

sult from this mechanism.

As a simple model for this process we consider a finite array composed of N ions of mass M . Each ion is connected to its neighbor by springs, and the surface of the array is free. The system has a set of $3N$ normal modes of oscillation. We denote the frequency of a mode by $\omega_{\vec{l}\lambda}$ where $\omega_{\vec{l}\lambda}$ is a solution of the secular equation $f(\omega_{\vec{l}\lambda}) = 0$. Here \vec{l} represents one of the vectors in reciprocal space which take discrete values fixed by boundary conditions and λ is the polarization. We also assume each mode experiences a linear viscous damping characterized by a damping factor $\gamma_{\vec{l}\lambda}$. If a periodic force is applied to certain (surface) ions in the array, then some or all of the normal modes can be excited. The excitation of a given mode depends both on the driving frequency ω and on how well the symmetry of the mode matches the symmetry of the applied force.

Let x_i denote the i th ionic coordinate ($i = 1, \dots, 3N$) and F_i the force component on that coordinate. Letting $l = (\vec{l}, \lambda)$, the l th normal coordinate ξ_l , and the generalized force Q_l , acting on ξ_l are related to x_i and F_i by

$$x_i = a_{ii}\xi_i, \quad (1)$$

$$Q_l = F_i a_{il}, \quad (2)$$

where the a_{il} are the matrix elements of the transformation to normal coordinates.⁹ The average power dissipated by the system is

$$\langle P \rangle = \frac{1}{2M} \sum_{l=1}^{3N} \frac{|Q_l|^2 \gamma_l \omega^2}{(\omega_l^2 - \omega^2)^2 + \gamma_l^2 \omega^2} \quad (3)$$

or in terms of the forces F_i

$$\langle P \rangle = \frac{1}{2M} \sum_{l=1}^{3N} \sum_{j=1}^{3N} \sum_{i=1}^{3N} \frac{F_i a_{il} F_j a_{jl} \gamma_l \omega^2}{(\omega_l^2 - \omega^2)^2 + \gamma_l^2 \omega^2} \quad (4)$$

Rice, Schneider, and Strässler⁸ have shown that electric fields only penetrate a few angstroms into metallic particles. Thus the i and j sums in Eq. (4) reduce to sums over surface ions. For simplicity we also assume that the field is the same everywhere in the surface region, and write

$$\sum_i \sum_j \text{surface} a_i a_{ji} = \frac{N_s C(\omega_i)}{3N}, \quad (5)$$

where N_s is the number of surface ions affected by the force and $C(\omega_i)$ accounts for the effectiveness of a uniform force acting only on surface ions in exciting each mode. The exact form of $C(\omega_i)$ depends on details of the particle surface and would be difficult to calculate. Our analysis of $C(\omega_i)$ is not complete, but for a continuous string driven by a force acting as a δ function on one end it turns out to be unity for all frequencies. When the discreteness of the string (i.e., it is made up of individual ions) is taken into account, then $C(\omega_i)$ falls off as frequency increases. In other cases it may also fall off and could affect our conclusions. For the moment we will take it to be unity up to the Debye cutoff.

With these approximations, and changing to a continuous representation in Eq. (4) we find

$$\langle P \rangle = \frac{(ZeE)^2}{2M} 4\pi r^2 t \rho \int_0^\infty \frac{D(\omega_i) \gamma_i \omega^2}{(\omega_i^2 - \omega^2)^2 + \gamma_i^2 \omega^2} d\omega_i. \quad (6)$$

Here the force in the surface region has been taken as ZeE with Z the effective charge of the ions. The number of surface ions is given by the number density ρ multiplied by the volume $4\pi r^2 t$ of the surface shell of thickness t . The density of phonon states $D(\omega_i)$ has been normalized so that

$$\int_0^\infty D(\omega_i) d\omega_i = 1. \quad (7)$$

The average power dissipated per unit volume in a sample containing G spheres per unit volume is $G\langle P \rangle$. The filling factor f of Ref. 1 is related to G for spheres of volume V by

$$G = f/V = 3f/4\pi r^3. \quad (8)$$

Finally the absorption coefficient α due to this mechanism is obtained by dividing by the intensity of incident radiation.

$$\alpha = \frac{12\pi(Ze)^2 t \rho f}{Mrc} \int_0^\infty \frac{D(\omega_i) \gamma_i \omega^2}{(\omega_i^2 - \omega^2)^2 + \gamma_i^2 \omega^2} d\omega_i \quad (9)$$

or

$$\alpha = AI(\omega).$$

The prefactor A is estimated using bulk aluminum values for M and ρ , and $Z=3$ (since aluminum was used in Ref. 1). Taking $t=3 \text{ \AA}$ and with the radius r in centimeters

$$A = 10^{11} f/r \text{ (cm sec)}^{-1}. \quad (10)$$

To estimate γ_i (which depends on the frequency ω_i) we use the expression for the attenuation of a

sound wave passing through a free electron gas. If the electron mean free path Λ is limited by the particle diameter, then for most of the spectrum the ratio of Λ to phonon wavelength is large, $\Lambda q \gg 1$, and the ultrasonic absorption coefficient¹⁰ can be written as

$$\alpha_u = CmZ\Lambda q/M\tau c_s, \quad (11)$$

where C is a constant on the order of 0.5 (it depends on phonon polarization), m is the electron mass, and τ the electron mean free time related to Λ by $\Lambda = \tau v_F$ where v_F is the velocity of an electron at the Fermi surface. c_s is the velocity of sound. The phonon damping is then given by

$$\gamma_i = \alpha_u c_s.$$

If γ_i is small the major contribution to the integral in Eq. (9) will come from ω_i near the infrared frequency ω or

$$c_s q \approx \omega.$$

Then

$$\gamma_i/\omega \approx CZ\hbar k_F/Mc_s. \quad (12)$$

Using $k_F = 1.75 \times 10^8 \text{ cm}^{-1}$ and $c_s = 5 \times 10^5 \text{ cm/sec}$ we find

$$\gamma_i/\omega \approx C \times 2.3 \times 10^{-2}$$

which is indeed small. The fact that γ_i/ω is small is of greater importance than its exact value.

The integral $I(\omega)$ of Eq. (9) can now be evaluated once $D(\omega_i)$ is known. Gilat and Nicklow¹¹ found the phonon density of states for bulk aluminum. Since the local density of states is known to attain the bulk form within one or two atomic layers from a surface we adopt their result as a reasonable approximation for the present calculation.¹² Figure 2 of Ref. 11 shows a large longitudinal phonon peak at $8.8 \times 10^{12} \text{ Hz}$ which corresponds to a wave number of 293 cm^{-1} which is well above the maximum frequency used in Ref. 1. We can approximate this peak by a δ function as appropriate for an Einstein spectrum. It gives a contribution to the absorption which is of the same order of magnitude as the GE or Drude model. If, however, one considers the broad transverse phonon portion of the spectrum considerable absorption results. Qualitatively it can be seen that as long as D/ω_i is slowly varying on the scale set by γ_i then $I(\omega)$ will mirror the phonon density of states. For the calculation we fit the transverse part by

$$\begin{aligned} D(\omega) &= (10^{-13}/D) 0.17\bar{\omega}^2, & 0 < \bar{\omega} < 2 \\ &= (10^{-13}/D) 0.49\bar{\omega}^2 (1 - 0.66\{1 - [(\bar{\omega} - 2)]^2/0.65\}^{1/2}), & 2 < \bar{\omega} < 2.65 \\ &= (10^{-13}/D) \{2.92 + [1.06(11.24 - 3.06\bar{\omega})^{1/2}]^2\}, & 2.65 < \bar{\omega} < 3.63 \\ &= (10^{-13}/D) \{3.42 - 2.25[1 - (5 - \bar{\omega}/1.37)^2]^{1/2}\}, & 3.65 < \bar{\omega} < 5. \end{aligned} \quad (13)$$

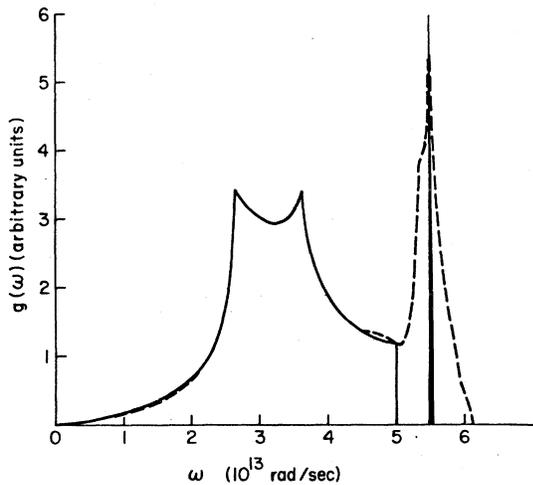


FIG. 1. Phonon density of states as a function of frequency. The solid curve shows the bracket portion of Eq. (13) which is our fit to the density of states of Gilat and Nicklow, Ref. 11. (Their result is shown by the dashed curve where it is distinguishable from the fitted curve.)

Here $\tilde{\omega} = \omega 10^{-13}$ and the constant \bar{D} is chosen so that the entire density of states (including the longitudinal peak which is taken as contributing $\frac{1}{3}$) is normalized to unity as per Eq. (7). We find $\bar{D} \approx 10$. The spectrum of Gilat and Nicklow and our fit to it are shown in Fig. 1. The absorption calculated from Eq. (9) for particle radius $r = 2.5 \times 10^{-7}$ cm and filling factor $f = 0.015$ is shown in Fig. 2. For comparison, the absorption observed in Ref. 1 for particles of this size rises quadratic-

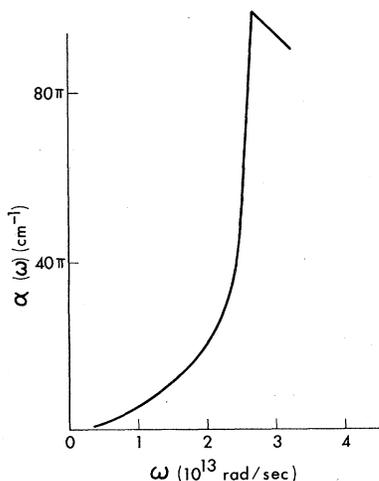


FIG. 2. Infrared absorption by small aluminum particles of radius 250 nm and filling factor $f = 0.015$ as calculated from Eq. (9).

ally and is approximately 9 cm^{-1} at $\omega = 1.89 \times 10^{13}$ Hz (100 cm^{-1}). The measurements were carried out up to about $\omega = 2.6 \times 10^{13}$ Hz which is close to where the absorption should level out if the present mechanism plays a major role. The absorption predicted by GE theory is also quadratic, but only gives an absorption of $4.5 \times 10^{-3} \text{ cm}^{-1}$ at 100 cm^{-1} which, as remarked previously, is three orders of magnitude too small.

The experiments reported in Refs. 1 and 2 find infrared absorption with the following properties: (i) a quadratic increase with frequency for wave number up to almost 150 cm^{-1} (with some possible structure at the highest frequencies); (ii) with magnitude $\alpha \approx 9 \times 10^{-4} \bar{\nu}^2 \text{ cm}^{-1}$ for $f = 0.015$, $r \approx 2.4 \text{ nm}$, and $\bar{\nu}$ in cm^{-1} ; (iii) the absorption increases as the particle radius increases. The GE theory predicts (a) a quadratic increase in absorption for any experimentally attainable distribution of particle sizes; (b) with $\alpha \approx 4.5 \times 10^{-7} \bar{\nu}^2$, which is much weaker than the observed values; and (c) a decrease of absorption with radius (as $1/r$). The theory presented in the present paper gives absorption of the same order of magnitude as observed in the experiments. However, it also displays the $1/r$ fall off of absorption with particle radius. An alternative theory has been put forward by Šimánek¹³ which does predict the correct order of magnitude of absorption, a quadratic frequency dependence, and a weak increase of absorption with increasing particle size. The Šimánek theory, however, pictures the experimental sample as a collection of long cylinders of amorphous insulating material in each of which there is embedded a cubic lattice of small metal particles. Since, for infrared frequencies, the dielectric constant of the metallic regions is much larger than that of the insulator, the field is excluded from the metallic regions, and the absorption occurs primarily in the insulating regions. For larger metallic particles the field is excluded from a greater portion of the medium giving rise to a stronger field in the insulator and stronger absorption. While the Šimánek results are in better agreement with the observed size dependence it is not clear whether it provides an accurate representation of the actual sample composition. Granquist and Buhrman¹⁴ have reported on their sample preparation techniques and their attempts to produce well isolated Al particles. The applicability of the Šimánek theory depends on how well they succeeded and where in the sample the absorption actually occurs.

The theory presented in the present paper applies to well-separated metallic particles which can have oxide coatings, but between which there is no connected absorbing medium. We find strong

absorption due to direct coupling of infrared radiation to the phonon modes via the unscreened surface ions. This mechanism may or may not be the dominant one in the experiments reported in Refs. 1 and 2. In particular it suggests a different dependence on particle size than indicated by the experiments. Also the role of the coupling function $C(\omega_i)$ of Eq. (5) is not yet completely understood. Nevertheless, our results indicate that this mechanism should show up in a sample of well-separated metallic particles and its presence could be observed by extending the experiments through a frequency range where there is a marked variation in the phonon density of states. Indeed such experiments appear to provide a good

means of gaining information about the phonon density of states in small particles. If the absorption does occur in the insulating material as suggested by Šimánek then the spectrum should also exhibit a phonon structure, but now the structure would be characteristic of the insulating material rather than the metal. Thus the extension of these experiments to higher frequencies should also provide information about the nature of the absorbing medium.

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