

such an experiment is very difficult at present because of the short time scales involved ( $\sim 10^{-13}$  sec $^{-1}$ ).

Finally we should also point out that the LO-phonon Raman modes in CdSe do not show the same behavior as the peak  $M$  and this is consistent with our theory. The LO phonon is not expected to couple strongly the  $A$  and  $B$  excitons with the  $C$  exciton because of the wave-vector dependence of the Fröhlich interaction.<sup>10</sup> The momentum of the LO phonon involved will be too large compared with the reciprocal of the exciton radii which are  $\approx 50$  Å in CdSe. However, we did observe enhancement of the LO-phonon Raman scatterings in the vicinity of the  $C$  exciton in CdSe and these results can be interpreted in terms of the  $C$  exciton alone.

One of the authors (P.Y.Y.) is indebted to Professor L. M. Falicov for enlightening discussions, especially for suggesting the idea of a strong coupling between the  $C$  exciton and the large-momentum  $A$  and  $B$  excitons. We are also grateful to Dr. Y. Petroff for the CdSe platelets used in this experiment, to J. A. Bradley for his expert technical assistance, and to Dr. F. Stern for critical reading of the manuscript.

<sup>1</sup>Another way to distinguish RS from PL is by the

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## Far-Infrared Absorption in Ultrafine Al Particles\*

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(Received 17 May 1976)

The first far-infrared measurements on metallic particles with diameters  $< 10$  nm are reported. The absorptivity is well approximated by  $\alpha_{\text{exp}} \approx C_{\text{exp}} \tilde{\nu}^2$ , where  $3 < \tilde{\nu} < 150$  cm $^{-1}$ . The results are compared with the Gor'kov-Eliashberg (GE) theory of particles with quantized electronic levels as well as with the classical Drude theory. When a size distribution is included,  $\alpha_{\text{GE}} = C_{\text{GE}} \tilde{\nu}^2$  irrespective of level statistics. However,  $C_{\text{exp}} \gg C_{\text{GE}}$  and the observed dependence on the diameter is directly contrary to predictions of the GE theory. Neither can the data be reconciled with the classical theory.

About a decade ago Gor'kov and Eliashberg (GE) published a theory of the electromagnetic properties of minute metallic particles due to a quantized conduction band.<sup>1</sup> One conspicuous re-

sult was the prediction of a periodic frequency dependence of the electronic susceptibility for a set of particles of equal size. If observed unambiguously this would uncover a unique test of ba-

sic assumptions for the energy-level statistics. Earlier measurements<sup>2</sup> by some of the present authors on far-infrared absorption in small Al particles showed some indications of a multiple-peak structure which was tentatively interpreted in terms of the GE model. Advances<sup>3</sup> in sample fabrication, where smaller and better characterized particles can be produced, have allowed us to undertake a more definitive check of the applicability of the GE theory. Here we report on some of the new measurements and give an analysis based on the GE equations. The most important experimental result is that no reproducible peaks in the frequency-dependent absorptivity of Al particles could be observed in spite of the considerable efforts expended. This fact may be in accord with the theory for any of the three statistical ensembles considered by GE provided proper account is taken of (unavoidable) size distributions, but *the absolute magnitude and the dependence on particle size of the observed absorptivity are in severe disagreement with theoretical predictions.*

Individually isolated Al particles were produced by inert-gas evaporation from an oven; the technique has been discussed in detail in Ref. 3. The volume fraction of metal (the "filling factor"  $f$ ) was on the order of a few percent. An experimental size histogram, determined by electron microscopy, is given in the inset of Fig. 1. It is compared with a log-normal distribution where the number of particles  $\Delta n$  per logarithmic diameter interval  $\Delta(\ln x)$  is  $\Delta n = f_{LN}(x) \Delta(\ln x)$  with

$$f_{LN}(x) = \frac{1}{(2\pi)^{1/2} \ln \sigma_g} \exp \left[ -\frac{1}{2} \left( \frac{\ln(x/\bar{x}_M)}{\ln \sigma_g} \right)^2 \right]. \quad (1)$$

Here  $\bar{x}_M$  denotes the statistical median of the diameters and  $\sigma_g$  is the geometric standard deviation. Figure 1 (inset) shows a calculated curve, where by using  $\bar{x}_M$  and  $\sigma_g$  as fitting parameters we get a function in very good correspondence with the experimental data. This agreement is in line with our previous experience on inert-gas-evaporated particles.<sup>3</sup>

The far-infrared transmission measurements were performed using both lamellar grating and Michelson interferometers.<sup>4</sup> The sample rotator and the <sup>3</sup>He-cooled germanium bolometer detector were both housed in the same <sup>4</sup>He cryostat.<sup>5</sup> The samples were constructed by clamping 2-mil polyethylene sheets onto a  $\frac{1}{2}$ -in.-diam brass ring which had been filled with the powder. At low frequencies in the far infrared where the powders were transparent we observed the Fabry-Perot

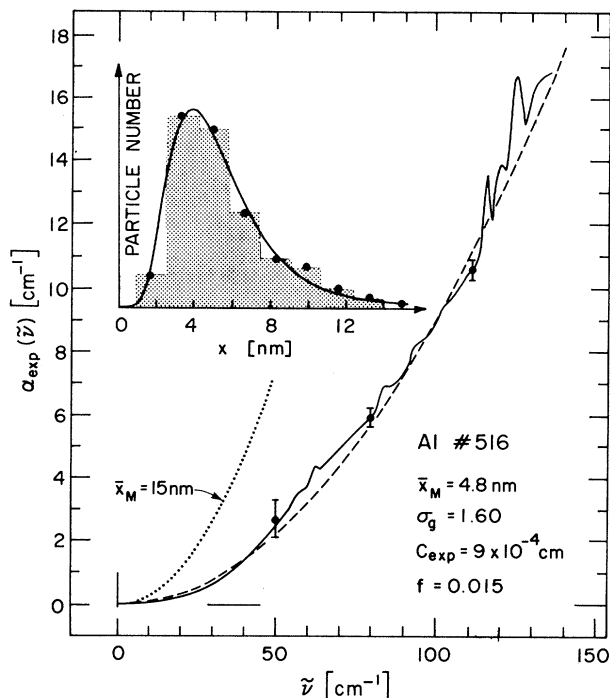


FIG. 1. The shaded region in the inset denotes a diameter histogram determined by dark-field electron microscopy on a random sampling of the particle specimen. The midpoints of the staples are indicated by dots. The particles were produced by evaporation in 1.5 Torr of pure Ar with addition of O<sub>2</sub>. The bell-shaped curve represents the log-normal distribution function with  $\bar{x}_M$  and  $\sigma_g$  as given in the figure. The solid curve in the main part of the figure reports the frequency-dependent absorption coefficient of the same sample. The error bars signify the reproducibility from one run to the next. The approximation of Eq. (2) yields the broken curve. The dotted curve shows an average variation of  $\alpha_{\text{exp}}$  for an Al specimen with  $\bar{x}_M = 15$  nm; these data are reproduced from Fig. 3 of Ref. 2.

fringes appropriate for two parallel polyethylene sheets separated by the brass-spacer thickness. In the frequency region where the sample showed significant absorption the fringes were not observed and we determined the absorption coefficient from a simple ratio measurement between powder samples of two different thicknesses  $l_1$  and  $l_2$ . In this case the absorption coefficient is  $\alpha_{\text{exp}}(\bar{\nu}) = (l_1 - l_2)^{-1} \ln [I_1(\bar{\nu})/I_2(\bar{\nu})]$ , where  $I$  signifies the intensity transmitted through the sample and  $\bar{\nu} \equiv 1/\lambda$  is the frequency of the radiation in wave number units.

The main part of Fig. 1 shows the measured frequency-dependent absorption coefficient. There is one adjustable parameter in the data shown in Fig. 1. When samples of different

lengths cause appreciably different amounts of far-infrared radiation to impinge on the detector, then the detector sensitivity is dependent on the sample length. This error shifts  $\alpha_{\text{exp}}$  by a constant amount independent of frequency. To remove this constant we set  $\alpha_{\text{exp}}$  equal to zero at zero frequency. The whole curve in Fig. 1 is well approximated by a parabola,

$$\alpha_{\text{exp}}(\bar{\nu}) = C_{\text{exp}} \bar{\nu}^2. \quad (2)$$

where  $C_{\text{exp}}$  is frequency independent. The peak structure reported earlier<sup>2</sup> for one sample with larger Al particles could *not* be established either in the sample of Fig. 1 or in others of similar mean diameters.

The experimental data will now be compared with the GE theory. Basic to the theory is the notion of quantized electronic levels at low temperatures when the particle sizes are sufficiently small. If the levels are completely nondegener-

ate<sup>6</sup> the average energy splitting is the inverted single-spin density of states at the Fermi level, i.e.,  $\Delta = 12\hbar^2\pi/m^*k_F x^3$ , where  $m^* \equiv \Lambda m$  is the thermal effective mass of the electrons and  $k_F$  is the Fermi wave vector. The distribution of statistically independent energy eigenvalues can be worked out from the general mathematical theories of random matrices<sup>7</sup>; three different statistical ensembles (orthogonal, symplectic, and unitary) may be applicable depending on the symmetries of the set of Hamiltonian matrices. For our purposes the most important result of the GE theory is their derivation of the electronic susceptibility,<sup>8</sup> which can be written as

$$\chi = \Lambda k_F x^2 / 20\pi^2 a_B + 139\Lambda A(\eta) / 1200\pi^2 a_B k_F \quad (3)$$

for boundary scattering of the electrons. Here  $a_B$  denotes the Bohr radius, and the factor  $A(\eta)$ , which depends on the approximate level statistics, is given by

$$A^{\text{orth}}(\eta) \equiv A^{\text{orth}}(\zeta) = 2 - \zeta^{-1} \sin 2\zeta - 2\zeta^{-1} \text{Ci}(\zeta)(\sin \zeta - \zeta \cos \zeta) + i [2\zeta - \zeta^{-1} + \zeta^{-1} \cos 2\zeta - \zeta^{-1} \text{Si}(\zeta)(\sin \zeta - \zeta \cos \zeta)], \quad (4)$$

$$A^{\text{sympl}}(\eta) \equiv A^{\text{sympl}}(z) = 2 - (2z)^{-1} \sin 2z - (z^{-1} \cos z + \sin z) [\text{Si}(z) + \pi/2] + i \{z - z^{-1} \sin^2 z - (z^{-1} \sin z - \cos z) [\text{Si}(z) + \pi/2]\}, \quad (5)$$

for the orthogonal and symplectic ensembles, which should apply when the atomic spin-orbit coupling is weak or strong, respectively. In Eqs. (4) and (5) the notation  $z = 2\zeta = (2\pi)^2 \hbar c \bar{\nu} / \Delta$  is used and Si (Ci) denotes the sine integral (cosine integral) function.

For our specimens  $\bar{\nu}^{-1} \gg x$ , implying that an effective dielectric permeability describes the electromagnetic properties. Empirically the filling factor  $f$  is small and hence the well-known Maxwell-Garnett<sup>9</sup> approach can be used. For a sample characterized by a size distribution one gets

$$\bar{\epsilon} = \frac{1-f + 3 \sum_j f_j \epsilon_j / (\epsilon_j + 2)}{(1-f) + 3 \sum_j f_j / (\epsilon_j + 2)}, \quad (6)$$

where the subscript  $j$  denotes particles belonging to the  $j$ th column in a size histogram and  $\epsilon_j = 1 + 4\pi\chi_j$ . The size distribution is specified in terms of a set of fractional filling factors,  $f_j$ , normalized by  $\sum_j f_j = f$ . When  $\bar{\epsilon} \equiv \bar{\epsilon}_1 + i\bar{\epsilon}_2$  is known, the absorptivity is obtained from

$$\alpha_{\text{GE}} = 2\pi \bar{\nu} [2(\bar{\epsilon}_1^2 + \bar{\epsilon}_2^2)^{1/2} - 2\bar{\epsilon}_1]^{1/2}.$$

This relation neglects energy dissipation due to eddy currents, which is justified in the GE theory for the size range  $x \lesssim 10$  nm and frequency range

$\bar{\nu} \lesssim 100 \text{ cm}^{-1}$ .

Equations (3)–(6) constitute a complete scheme to calculate far-infrared absorptivity within the GE theory. Results from a set of computer runs for particles with  $\bar{x}_M = 2.5$  nm are contained in Fig. 2. When all particles have identical size ( $\sigma_g = 1$ ) a strongly oscillatory absorptivity is predicted for the symplectic ensemble, whereas the orthogonal ensemble displays a much smoother curve. The peak structure is very sensitive to the occurrence of size distributions, and even at  $\sigma_g = 1.1$  an essentially structureless curve is encountered; moreover, the same curve is obtained for the two ensembles. Empirically, inert-gas-evaporated particles consistently have standard deviations in the range<sup>3</sup>  $\sigma_g = 1.48 \pm 0.12$  and the corresponding interval for islands in discontinuous films is<sup>3</sup>  $\sigma_g = 1.28 \pm 0.06$ . In fact, we do not know of *any* technique to prepare ultrafine particles which is capable of yielding  $\sigma_g$ 's as small as 1.1! Hence we are forced to conclude that *the multiple absorptivity peaks, allowing an experimental way to separate between different ensembles, cannot be observed in practice.*

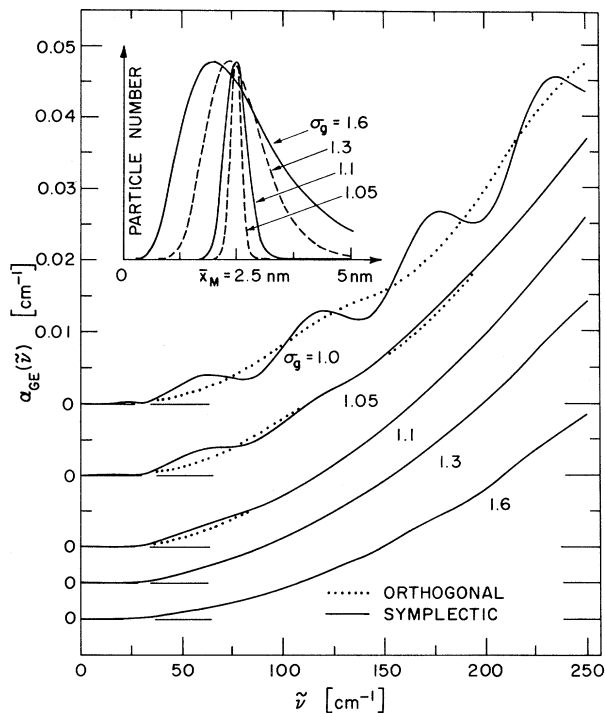


FIG. 2. Absorptivity versus frequency for the orthogonal and symplectic ensembles calculated for log-normal size distributions with five different values of  $\sigma_g$  (cf. the inset). The curves are displaced vertically by 0.01 or 0.005  $\text{cm}^{-1}$ . We used the values  $k_F = 1.75 \times 10^8 \text{ cm}^{-1}$ ,  $\Lambda = 1.48$ , and  $f = 0.02$ .

For  $\sigma_g \gtrsim 1.1$  and  $\bar{x}_M \gtrsim 2.5 \text{ nm}$  one is justified in setting  $A^{\text{orth}}(z) = A^{\text{symp}}(z) = iz$  in Eqs. (4) and (5). It can then be shown that for aluminum

$$\alpha_{\text{GE}}(\tilde{\nu}) \approx C_{\text{GE}} \tilde{\nu}^2, \quad (7)$$

with  $C_{\text{GE}} = 9.64 \times 10^{-5} f \langle x^{-1} \rangle$ . Here  $\tilde{\nu}$  is in units of inverse centimeters and  $x$  in nanometers. The average  $\langle \rangle$  is to be taken over the size histogram. The frequency dependence in Eq. (7) is the same as that experimentally observed. However calculations of  $C_{\text{GE}}$  for the particles of Fig. 1 yield  $C_{\text{GE}} = 4.5 \times 10^{-7} \text{ cm}$ , while experimentally  $C_{\text{exp}} = 9 \times 10^{-4} \text{ cm}$  (cf. Fig. 1) which illustrates the consistently<sup>10</sup> occurring inequality

$$C_{\text{exp}} \gg C_{\text{GE}}.$$

An equally serious discrepancy with the GE theory is found in the size dependence of the absorptivity. From the dotted line in Fig. 1, representing the measured averaged  $\alpha_{\text{exp}}(\tilde{\nu})$  for a specimen with  $\bar{x}_M = 15 \text{ nm}$ , we find that the absorptivity is higher for samples consisting of larger particles. This is counter to the variation predicted from the GE theory which yields  $\alpha_{\text{GE}} \propto \bar{x}_M^{-1}$  from the

above equations.

As an alternative to the GE theory the experimental results can also be compared to the far-infrared absorptivity as calculated in the context of the classical Drude theory. With this classical theory, if boundary scattering of the conduction electrons is assumed, it can be shown that for aluminum  $\alpha_D(\tilde{\nu}) \approx 7.48 \times 10^{-5} f \langle x^{-1} \rangle \tilde{\nu}^2$  for  $x \lesssim 5 \text{ nm}$  and  $\alpha_D(\tilde{\nu}) = 4.68 \times 10^{-8} f \langle x^{-3} \rangle \tilde{\nu}^2$  for  $x \gtrsim 5 \text{ nm}$ . Hence the parabolic frequency dependence is forecast also by the classical theory; furthermore, the observed size dependence of  $C_{\text{exp}}$  is in qualitative agreement with the theoretical one. However, just as for the GE theory, the predicted absorption coefficients are orders of magnitude too small to be reconciled with the experimental data.

The main conclusion is that both the absolute magnitude and the size dependence of the measured absorptivity are in serious disagreement with the GE theory which proves convincingly that it does not provide an adequate description of the far-infrared data. The classical Drude theory is also found to be incapable of directly explaining the results.

We acknowledge informative discussions with Professor D. B. Tanner. The computer programming was performed by Mr. M. Bastuschek.

\*Research supported by the National Science Foundation Grant No. DMR 74-02609, by the U. S. Energy Research and Development Administration under Contract No. AT (11-1)-3151, Technical Report No. C00-3151-66, and by National Science Foundation—Research Applied to National Needs Grant No. AER 75-22772. Additional support was received from the National Science Foundation under Grant No. GH-33637 through the Cornell University Materials Science Center.

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values are about two orders of magnitude too high. This results from using a small  $k_F$  and having an incorrect prefactor for the static susceptibility in the GE theory.

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## COMMENTS

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### Comment on Evidence for Primordial Superheavy Elements\*

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(Received 7 July 1976)

We report on  $\gamma$  rays which could interfere with the observation of x rays from the super-heavy element 126.

Photon energy spectra from proton bombardment of monazite inclusions in biotite mica have been interpreted as evidence for the presence of relatively stable superheavy nuclei.<sup>1</sup> In a continuing effort to clarify our understanding of the results, we have measured the x rays and  $\gamma$  rays in the energy range from 10 to 100 keV for proton bombardment of all the stable naturally occurring elements  $Z \geq 9$ , except the noble gases, in a manner similar to that of Gentry *et al.*<sup>1</sup> The results of this search are being prepared for publication elsewhere. It is the purpose of this Comment to note that one  $\gamma$  ray has been found which can interfere with the observation of one of the elements reported in Ref. 1. Other possible x-ray interferences have been discussed in Ref. 1.

Naturally occurring elemental targets were prepared by gluing pure samples with a polystyrene and benzene mixture to thin Mylar backings. Usually the chemical form of the target was the oxide of the element although many of the targets were of the pure element. In general, the targets were "thick" and the 5.7-MeV proton beam used in the search was often nearly stopped in the target. The x and  $\gamma$  radiation emerging from the target were detected by a Si(Li) x-ray detector<sup>1</sup> after passing through a thin Plexiglas chamber window, a thin beryllium detector window, and an 813- $\mu$ m aluminum absorber. Beam currents were held to low levels (usually of the order of  $10^{-9}$  A) so that the total counting rate in the x-ray detector was always less than  $500 \text{ sec}^{-1}$ .

The x radiation expected from each target was properly identified in every case and could be used to calibrate the detection system. The x

rays for the lighter elements were not observed because of the absorber arrangement used. Numerous  $\gamma$  rays were observed and were identified in many cases as those coming from  $(p, n\gamma)$  reactions in the target. Identification of several of the  $\gamma$  rays is not yet completed. The  $\gamma$  ray observed in this search, which can interfere with the observation of one of the  $L\alpha_1$  x rays reported in Ref. 1, is the  $(27.23 \pm 0.03)$ -keV transition in <sup>140</sup>Pr, produced by means of the reaction <sup>140</sup>Ce( $p, n$ )<sup>140</sup>Pr. This transition is not reported to have been observed directly but could occur between the known levels of <sup>140</sup>Pr.<sup>2</sup> The isotopic identification was made by using a thick target prepared in the manner described above with oxide enriched to 99.7% in <sup>140</sup>Ce. The isotopic target was also free of the trace contaminants present in some of the elemental targets. Figure 1 shows a portion of the spectrum obtained at three different bombarding energies from the <sup>140</sup>Ce oxide target. The proton beam energy was varied in order to measure the energy dependence of the  $\gamma$ -ray yield. The spectra are normalized to equal numbers of counts in the Ce  $K\alpha_{12}$  x-ray peak in the spectrum, since the beam was stopped in the target. The three spectra demonstrate that, as expected for a  $(p, n)$  reaction excitation function in this mass and energy region, the 27.23-keV  $\gamma$ -ray intensity rises much more rapidly with energy than the x-ray intensity.

The energy of the observed  $\gamma$  ray is almost identical to that reported in Ref. 1 for the  $L\alpha_1$  transition of a superheavy element with  $Z=126$ . Since cerium is one of the major constituents of the monazite inclusions,<sup>1</sup> this  $\gamma$  ray must be re-