Size quantization of acoustic phonons in microcrystals surrounded by an elastic matrix

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In analyzing the effect of an elastic glassy matrix on the acoustic vibrations of microcrystals we discovered and confirmed by means of low-frequency Raman scattering that new surface vibrations appear when microcrystals are embedded in a matrix. These vibrations, which are due to the appearance of a restoring force during the rotation of the microcrystals, participate in the low-frequency Raman scattering observed in a number of studies [Phys. Rev. B **47**, 1237 (1993); Phys. Rev. B **44**, 6243 (1991); JETP Lett. **47**, 298 (1988); JETP Lett. **48**, 678 (1988)]. It is shown that the effect of the matrix cannot be ignored, even in the case where the Lamé constants and the density of the microcrystal are substantially different from those of the matrix. © *1995 American Institute of Physics.*

In semiconductor nanocrystals both the electronic and vibrational energy levels are discrete because the motion is limited in three directions. As the microcrystal becomes smaller, phonons with large wave vectors become involved in the electron-phonon interaction and the scattering of the charge carriers by the acoustic phonons become stronger than scattering by the optical phonons. For example, in Ref. 1 it was discovered that the interaction of size-quantized electrons and acoustic phonons in microcrystals is responsible for the decay rate of excitonic polarization. It was found that the discrete acoustic energy levels in nanocrystals can be recorded with the aid of low-frequency Raman scattering in the region of the spectrum ≈ 10 cm^{-1}; this was first achieved in Ref. 2. Since then a number of papers on low-frequency Raman scattering by different microcrystals embedded in glassy matrices have been published.[3–6] In all of these works, which were based on the fact that the Lamé constants λ and μ and the density ρ of the microcrystals differ substantially from those of the matrix, the experimental data are interpreted on the basis of the assumption that the surface of the microcrystals is free.

In the present paper we analyze the effect of an elastic glassy matrix on the spherical and torsional vibrations of microcrystals and we give on the basis of this analysis a new interpretation of the low-frequency Raman scattering spectra. We investigated heterophase systems consisting of Ge microcrystals embedded in a glassy GeO$_2$ matrix. These systems are described in Ref. 5. The Raman scattering spectra were measured in

the 90-degree scattering geometry on a Jobain Yvon U-1000 spectrometer using the 514.5 and 647.1-nm excitation lines of Ar^+ and Kr^+ lasers. To determine the role of the boundary conditions, other chemical compositions of the microcrystals and matrices with different elastic constants and densities, obtained in Refs. 3 and 4, were also studied. It was found that when the microcrystals are embedded in a matrix, new surface vibrations arise as a result of the appearance of a restoring force that limits the free rotation of the microcrystals. Apparently, these vibrations participate in the low-frequency Raman scattering observed experimentally in several studies.[3–5,7] It was also found that the effect of the matrix cannot be neglected, even when the Lamé constants λ and μ and the density ρ of the microcrystals are substantially different from those of the matrix.

In Ref. 8 it was shown that according to the selection rules for Raman scattering by spherical particles, only spheroidal modes with even angular momentum can be observed in the spectra. In practice, however, the microcrystals grown in a transparent matrix ordinarily are not perfectly spherical. In this case the selection rules break down and torsional vibrations with odd angular momentum should also be observed in the spectra. According to Ref. 9, the characteristic frequencies of the torsional vibrations of microcrystals embedded in a glassy matrix can be determined from the equation

$$D_m^T = 0, \tag{1}$$

where D_m^T is the determinant of a 2×2 matrix whose components are presented in Ref. 7. Figures 1a and 1b show, respectively, the shift of the characteristic frequencies v_{nl}^T of the torsional vibrations and the distribution of the displacement amplitude u and the energy density $u^2 R^2$ of the surface mode over the radius of the microcrystal with increasing stiffness of the matrix, i.e., with increasing ratio C_1/C_2 for fixed C_2. Here $C_1 = (\mu_m/\mu_i)^{1/2}$, $C_2 = (\rho_m/\rho_i)^{1/2}$, μ is the shear modulus, ρ is the density, the index m refers to the matrix, the index i refers to the microparticle, $v_{nl} = \eta_{nl} v_t / \pi d c$ is the linear frequency for the (n,l) vibrational mode characterizing the position of the maximum of the Raman scattering spectrum, η_{nl} is a dimensionless frequency, n is the number of the harmonic, l is the angular momentum, d is the diameter of the microcrystal, v_t is the transverse velocity of sound, and c is the speed of light. It is evident from Fig. 1a that the surface torsional mode with angular momentum $l = 1$ is absent in microcrystals with a free surface (dashed curves), since it corresponds to the rotation of the crystal as a whole. If the crystal is embedded in a matrix, then, as one can see from Fig. 1a (solid curves), a solution appears for the surface mode with angular momentum $l = 1$. This discrete level arises because a restoring force that does not permit the crystal to rotate freely appears. In addition, it is evident from Fig. 1 that in the presence of the matrix, as its stiffness increases, the characteristic frequencies of the surface vibrational modes ($n = 0$) increase for all l and the maximum of the displacement amplitude shifts into the microcrystal. The same situation occurs with the internal vibrational modes ($n \geq 1$), as pointed out previously in Ref. 7. In Ref. 9, the authors incorrectly concluded that the matrix has the opposite effect — the surface vibrational mode vanishes and the internal torsional vibrational modes are softened. Therefore, the frequency v_1^T of the maximum of the Raman scattering spectrum for the surface torsional mode with angular momentum $l = 1$ for crystals embedded in a matrix is not equal to $1.83 \cdot v_t / dc$ (Refs. 3 and 4), as would happen in the case of a microcrystal with a free surface, since in the presence of a matrix
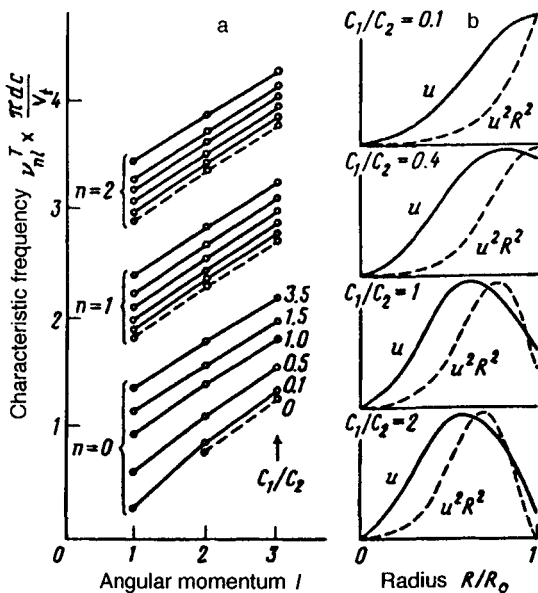
FIG. 1. a — Shift of the characteristic frequencies of torsional vibrations of a microcrystal for surface ($n = 0$) and internal ($n \geqslant 1$) modes with increasing stiffness of the matrix, i.e., with increasing ratio C_1/C_2; for this example $C_2 = 0.77$. For clarity, the discrete values of the frequencies for different angular momenta are connected by lines. b — Distribution of the displacement amplitude u and the energy density u^2R^2 of the surface mode along the radius of the microcrystal for different values of C_1/C_2.

there appears a new solution for the surface mode with $l = 1$, whose characteristic frequency increases, for example, from $0.2 \cdot v_t/dc$ to $1.4 \cdot v_t/dc$, as the stiffness C_1/C_2 of the matrix increases from 0.1 up to 3.5 (Fig. 1a).

The characteristic frequencies of the spheroidal vibrations of microcrystals embedded in a matrix are determined from the equation

$$D_m^S = 0, \tag{2}$$

where D_m^S is the determinant of a 4×4 matrix whose components are presented in Ref. 9. Here there are twice as many variables and parameters as in the case of torsional vibrations. Therefore, the effect of the matrix on the characteristic frequencies of the spheroidal vibrations of the microcrystal becomes more complicated.

It is generally accepted[3-6] that when the Lamé constants λ and μ and the density ρ of the matrix are substantially different from those of the microcrystal, the surface of the microcrystal can be regarded as virtually free. We believe on the basis of our results that this assumption is incorrect. The torsional surface modes do not vanish, even for approximately equal values of the parameters, and the Raman-active spheroidal surface modes $\nu_0^S(l=0)$ and $\nu_2^S(l=2)$ tend to vanish when the parameters λ, μ, and ρ differ substantially. For example, in the work by Tamura et al.,[9] the mode ν_0^S vanished in the
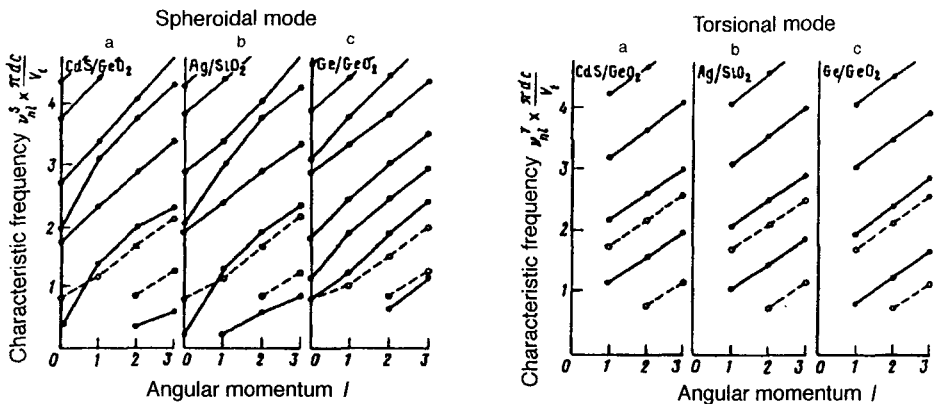
FIG. 2. Distribution of the characteristic vibrational frequencies for spheroidal modes A and torsional modes B of microcrystals embedded in glassy matrices. The frequencies were obtained by solving Eqs. (1) and (2). The dashed lines denote frequencies for a free surface of the crystal for $n=0$ and 1.

case of Pb microparticles in porous glass. It would have existed for $\mu_m \leqslant \mu_i$ ($C_1 \leqslant 1$), and for $\mu_m > \mu_i (C_1 > 1)$ the solution vanished even though all parameters for the matrix were substantially different from those of the microcrystal.

We now examine the interpretation given in Ref. 3 of the low-frequency Raman scattering spectra of CdS microcrystals embedded in a GeO_2 matrix. In this work the surface of the microcrystals was assumed to be free. The clearest spectra were obtained for microcrystals with $d=7.5$ nm, and the frequency of the maximum for depolarized scattering is equal to $\nu_{\parallel\perp}=7.1$ cm^{-1}. On the basis of their calculations the authors attributed this signal to a spheroidal surface mode with $l=2$. We checked the calculation for this case; the results are presented in Fig. 2a. As one can see from the figure, when the crystal was embedded in the matrix, the spheroidal surface mode with $l=2$ softened from $0.85 \cdot v_t/dc$ to $0.35 \cdot v_t/dc$ and its frequency became equal to 2.9 cm^{-1}, i.e., the authors of Ref. 3 could not observe it because of the strong diffuse scattering. This is most likely a torsional surface mode with $l=1$ which appeared when the crystal was embedded into the matrix. According to the figure, this frequency is equal to $\nu_1^T = 1.18 \cdot v_t/dc = 9.7$ cm^{-1}. If the fact that the spectra were recorded with strong diffuse scattering, which shifts the maxima of the peaks in the direction of low energies, is taken into account, then after the diffuse scattering is subtracted from the experimental spectrum, the position of the maximum should be shifted from 7.1 cm^{-1} to the theoretical value 9.7 cm^{-1}.

We now consider the case of Raman scattering from Ag microcrystals embedded in a SiO_2 matrix.[4] Here the surface of the microcrystals is also assumed to be free. In this work it was noted that for microcrystals which are larger than 4 nm, the agreement between theory and experiment is very poor. In the experimental spectra the maximum was equal to 14.2 cm^{-1} for 4.1 nm particles and 12.1 cm^{-1} for 5.2 nm particles. The authors assumed that these spectra are due either to the surface spheroidal modes with $l=0$ or $l=2$, since these spectra are partially depolarized. We checked the calculation for this case. The results are presented in Fig. 2b. One can see that the frequency ν_0^S softened
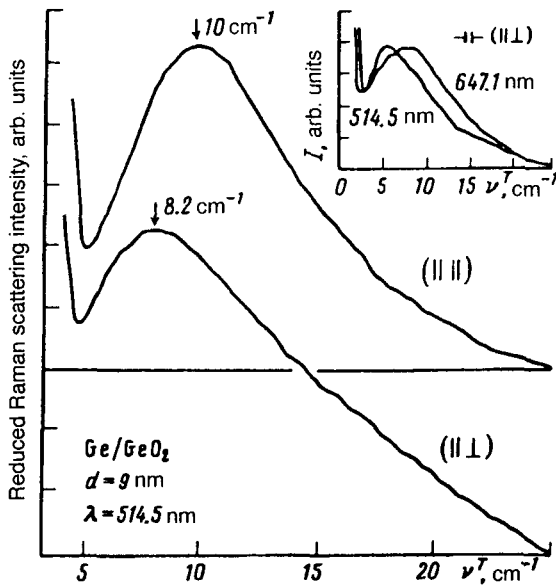
FIG. 3. Polarization dependence of the low-frequency Raman scattering spectra, normalized to the Bose–Einstein occupation factor, for Ge crystals with $d=9$ nm in a GeO$_2$ matrix. Inset: Low-frequency Raman scattering spectra from the same sample for two wavelengths of the exciting light.

from $0.78 \cdot v_t/dc$ to $0.2 \cdot v_t/dc$ and became equal to 2.7 cm^{-1} for particles with $d=4.1$ nm and 2.4 cm^{-1} for particles with $d=5.2$ nm. Therefore, these maxima cannot be observed, since they are masked by the diffuse scattering; the frequency v_2^S also behaves in approximately the same way. We can then assume that these oscillations are due to $l=1$ torsional surface modes which appear when the crystals are embedded in the matrix. As one can see from Fig. 2b, the frequency of the torsional mode is equal to $v_1^T = 1.11 \cdot v_t/dc$, which gives 15 cm^{-1} for particles with $d=4.1$ nm and 11.9 cm^{-1} for particles with $d=5.2$ nm, which are very close to the experimental values 14.2 cm^{-1} and 12.1 cm^{-1}.

Let us now examine our experimental data. We measured the low-frequency Raman scattering from Ge microcrystals in a transparent GeO$_2$ matrix. The spectra for particles with $d=9$ nm with different polarizations are shown in Fig. 3. We see that the maximum of the peak for polarized scattering ($\|\|$) is shifted to higher frequencies from the maximum with depolarized scattering ($\|\perp$). The computational results are shown in Fig. 2c. The frequency of the polarized peak is equal to the theoretical value for the spherical mode $v_0^S = 0.8 \cdot v_t/dc$. We know that depolarized scattering of light could be due either to spheroidal modes with angular momentum $l=2$ or torsional modes with $l=1$. To determine which of these modes participates in the scattering, we examined the low-frequency Raman scattering spectra recorded in Ref. 7, using the same sample with two wavelengths of the exciting light, 514.5 and 647.1 nm; these spectra are shown in the inset in Fig. 3. It turns out that the modes which lie deeper beneath the surface of the microcrystal and on which the more weakly absorbed light with $\lambda = 647.1$ nm is scattered have the

higher frequency. Therefore, the scattering occurs on the surface torsional modes with $l = 1$, because only their frequency increases continuously as the stiffness of the matrix increases and they are localized deeper beneath the surface of the crystal, as one can see from Figs. 1a and 1b. The scatter of the frequency of the surface mode is apparently associated with the nonuniformity of the conditions at the boundary between the microcrystal and the matrix. Scattering occurs precisely on the surface modes, since all internal modes with $n \geqslant 1$ for both spheroidal and torsional vibrations occur at much higher frequencies than the energy difference observed in the experiment, as one can see from Fig. 2c.

The experiments examined above show that in all cases the depolarized scattering is due to surface torsional modes with $l = 1$, which appear when microcrystals are embedded in a matrix. Moreover, it follows from the calculations that the matrix strongly influences the frequencies of the spheroidal and torsional vibrational modes, especially for $n = 0$ and 1 (see Fig. 2), even in the case where the Lamé constants λ and μ and the density ρ of the microcrystals differ substantially from those of the matrix.

In conclusion, we note that the electron-phonon interaction with the acoustic modes in small microcrystals occurs mainly via the deformation potential and is described by the term $E_d \cdot \mathrm{div}\ \mathbf{u}$, where E_d is the deformation potential, and $\mathbf{u}$ is the displacement vector.[1] If the particles were perfectly spherical, then the torsional modes would not contribute to this interaction because of their purely transverse character. When the microcrystals deviate from a spherical shape, their symmetry changes, the torsional modes become mixed, the selection rules for Raman scattering break down. As a result, it becomes possible to observe these modes experimentally.

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