

# Low-frequency Raman scattering by volume vibrations of microcrystals

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The low-frequency Raman scattering by germanium microcrystals as a function of the wavelength of the exciting light has been studied. This has been the first experimental demonstration and theoretical confirmation that surface vibrations of microcrystals are transformed into volume vibrations because of the elastic matrix that surrounds them.

Many of the anomalous thermal and electrical properties of microparticles are attributable to the influence of the surface and size effects on the phonon spectrum of these microparticles.<sup>1,2</sup> The study of the photon spectrum of microparticles therefore merits a closer scrutiny.<sup>3,4</sup>

We are now confronted with a contradictory situation. The theory<sup>3</sup> predicts that microparticles surrounded by an elastic insulator have no surface vibrational modes, while the experimental data<sup>5,6</sup> are interpreted in such a way that these modes are responsible for the low-frequency Raman scattering. We have established experimentally that surface vibration modes actually do not vanish and we have shown for the first time that bulk vibrations also participate in the low-frequency Raman scattering.

We have studied heterophase systems consisting of Ge microcrystals inside an amorphous GeO<sub>2</sub> insulator.<sup>7</sup> The Raman scattering spectra were recorded in the 90° scattering geometry on the "Ramanor U-1000" spectrometer with (||⊥) polarization; i.e., the depolarized scattering which can be attributed to only the torsional vibrational modes was observed.<sup>7,8</sup>

The natural frequencies of the torsional vibrational modes of the microcrystals surrounded by the matrix of an elastic insulator can be determined from the equation<sup>3</sup>

$$D \equiv \begin{vmatrix} \frac{l-1}{\eta_i} j_l(\eta_i) - j_{l+1}(\eta_i) & j_l(\eta_i) \\ C_1 C_2 \sqrt{\frac{\pi}{2\eta_m}} \left( \frac{l-1}{\eta_m} K_{l+1/2}(\eta_m) \right. \\ \left. - K_{l+3/2}(\eta_m) \right) \sqrt{\frac{\pi}{2\eta_m}} K_{l+1/2}(\eta_m) \end{vmatrix} = 0, \quad (1)$$

where  $j_l(\eta)$  is a spherical Bessel function of the second kind,  $\eta_{l,n} = \omega_{l,n} \bar{R} / v_t$  is a dimensionless frequency,  $\omega_{l,n}$  is the angular frequency associated with the  $(l,n)$ -th vibrational mode,  $l$  is the angular momentum which, according to the selection rules

for first-order Raman scattering, is equal to 2;  $n$  is the number of the harmonic,  $\bar{R}$  is the mean radius of the particle,  $\sqrt{\pi/2\eta}K_{l+1/2}(\eta)$  is a modified spherical Bessel function of the third kind,  $\eta_m = \eta_i v_{ti}/v_{tm}$ ,  $C_1 = (\mu_m/\mu_i)^{1/2}$ ,  $C_2 = (\rho_m/\rho_i)^{1/2}$ ,  $v_i$  is the transverse velocity of sound,  $\mu$  is the shear modulus,  $\rho$  is the density, the subscript  $m$  refers to the matrix, and the subscript  $i$  refers to the microparticle.<sup>1)</sup> Figure 1, a and b, shows respectively the shift of the normal vibrational modes and the distribution of the displacement amplitude and of the energy density of the surface mode along the radius of the microcrystal with an increase in the ratio  $C_1/C_2$  at a given value of  $C_2$ , i.e., with an increase in the stiffness of the matrix. We see that the surface vibrational mode ( $n=0$ ) in this case does not vanish: its natural frequency increases and the energy distribution maximum moves into the interior of the microcrystal. This situation also applies to the internal vibrational modes ( $n \geq 1$ ). Tamura *et al.*<sup>3</sup> concluded falsely that the action of the matrix leads to the inverse effect: to the disappearance of the surface vibrational mode and damping of the internal vibrational modes.

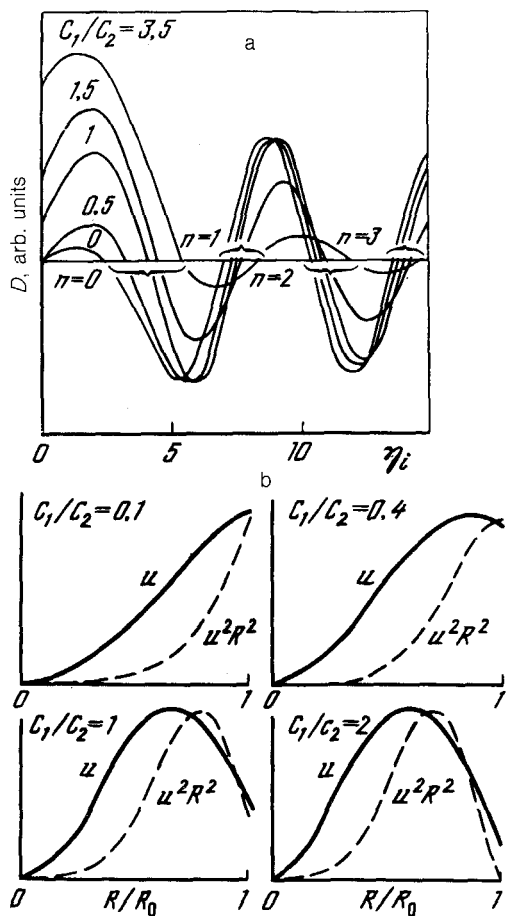


FIG. 1. (a) Graphic solution of Eq. (1). The braces denote the range over which the natural vibration frequencies vary in the case of the surface mode ( $n=0$ ) and the internal mode ( $n \geq 1$ ) for various values of  $C_1/C_2$ ,  $C_2 = 0.77$ ; (b) distribution of the displacement amplitude  $u$  and the energy density of the surface mode  $u^2 R^2$  along the radius of the microcrystal for various values of  $C_1/C_2$ .

To identify these effects, we recorded the Raman scattering spectra with two wavelengths of the exciting light, 5145 Å and 6471 Å (Fig. 2, a and b). Since the light with  $\lambda = 5145 \text{ \AA}$  is absorbed in a layer  $L \approx (2\alpha)^{-1} \approx 80 \text{ \AA}$ , where  $\alpha$  is the absorption coefficient of germanium, it excites principally the surface vibrational modes with  $n = 0$ . The proof of the fact that the Raman scattering spectrum in this case is attributable to the scattering in the surface layer is the agreement of the average dimensions of the microcrystals which were determined by two methods: from the frequency of its maximum  $\nu_{2,0}^{\text{max}} = 5.4 \text{ cm}^{-1} \approx 0.8v_1/2\bar{R}c$  (Ref. 5), where  $c$  is the velocity of light, which yielded  $2\bar{R} \approx 160 \text{ \AA}$ , and on the basis of the Scherrer formula,<sup>9</sup> from the half-width of the diffraction line obtained in the diffraction of x rays from the (220) planes at an angle  $2\theta = 45.3^\circ$ , which gave  $2\bar{R} \approx 165 \text{ \AA}$ .

The light with  $\lambda = 6571 \text{ \AA}$  makes it possible to detect Raman scattering at a depth  $L \approx 400 \text{ \AA}$ ; i.e., this light passes through the entire microcrystals and therefore must scatter from bulk vibrations. The difference spectrum b-a must therefore be determined exclusively by the bulk vibrations which have a high frequency and which are situated deeper than the surface vibrations, which account for the spectrum in Fig. 2a. Since in these vibrations, as usual,  $n = 0$  (since the vibrations with  $n \geq 1$  occur in the tail of the spectrum at  $\nu > 15 \text{ cm}^{-1}$  and their contribution is insignificant), we see even in this case the lowest-frequency vibrations which transform from surface vibrations to bulk vibrations as a result of the action of the elastic matrix (consistent with calculations; Fig. 1, a and b). The fact that the Raman scattering spectrum remains constant in the case of a strongly absorbed light (Fig. 2a) apparently suggests that the matrix of some of the microcrystals does not make a tight contact with the entire surface.

For comparison, we recorded similar Raman scattering spectra for two wavelengths of the exciting light (Fig. 3) for the silver halide microcrystals dispersed in a transparent glassy  $\text{SiO}_2\text{Ba}_2\text{O}_3$  matrix.<sup>8</sup> We see that the position of the maxima of the Raman scattering spectra, as expected, does not depend on the wavelength, since the silver halide particles are completely transparent in the visible range. We also see that each spectrum has components from the surface and bulk vibrational modes.

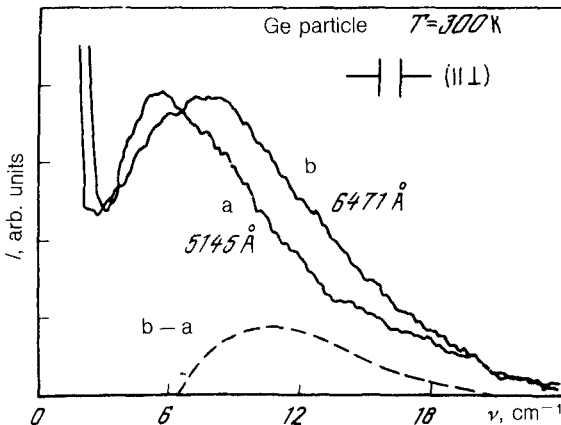


FIG. 2. Raman scattering spectra of the scattering by normal acoustical modes of Ge microcrystals for two wavelengths of the exciting light. The dashed curve represents the difference spectrum.

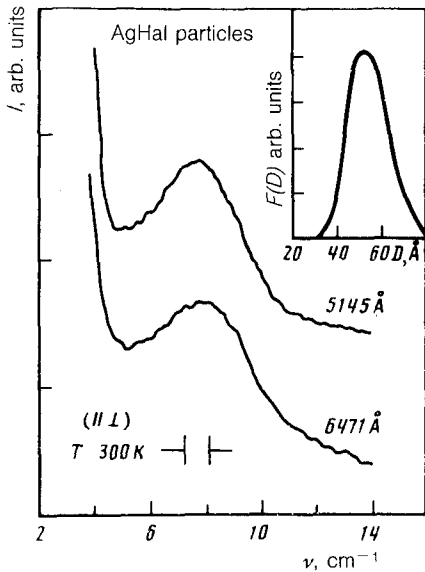


FIG. 3. Raman spectra for AgHal microcrystals. The inset shows the size distribution of particles found with the help of small-angle x-ray scattering.<sup>8</sup>

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In conclusion, we should like to make two points. First, the amount by which the frequency of the surface mode is shifted can be used to determine, from Eq. (1), the ratio  $C_1/C_2$  and hence the sound velocity in media for which the direct methods of measuring it cannot be used. For  $\rho_{\text{Ge}} = 5.33 \text{ g/cm}^3$ ,  $v_{l,\text{Ge}} = 3.25 \times 10^5 \text{ cm/s}$ , and  $\rho_{\text{GeO}_2} = 3.12 \text{ g/cm}^3$  the transverse sound velocity in  $\text{GeO}_2$  is, according to our data,  $4.6 \times 10^5 \text{ cm/s}$ . Secondly, the method of determining the size of microcrystals from the maximum of the low-frequency Raman-scattering spectrum proposed in Refs. 5, 6, and 8 may underestimate their size by 20–30% because of the disregard for the scattering by bulk vibrational modes. The microparticle size of  $\approx 40 \text{ \AA}$ , determined from the maximum of the Raman-scattering spectra in Fig. 3,  $\nu_{2,0}^{\text{max}} = 7.7 \text{ cm}^{-1}$ , evidently differs for this reason from the value of  $52 \text{ \AA}$ , at which the size distribution has a maximum.

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<sup>1</sup>In Ref. 3 the terms  $d_{21}$  and  $d_{22}$  for matrix (1) are incorrect.

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