Low-frequency Raman scattering by small semiconductor particles

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A study has been made of the spectra of the Raman scattering of light by germanium microscopic crystals dispersed in a transparent dielectric matrix of germanium dioxide. The results yield the first observation, in the Raman spectra of microscopic semiconductor crystals, of a low-frequency peak due to natural acoustic vibrations of the crystals.

It has recently been shown[1-4] that microscopic CuCl and CdS semiconductor crystals, which have been grown successfully in the interior of a transparent dielectric (glass) matrix, constitute a unique class of entities for a study of size effects by optical methods. In this letter we are reporting a technique for producing a new heterophase system consisting of microscopic Ge crystals inside a transparent amorphous dielectric, GeO_2. Experiments on this system have yielded the first observation of low-

frequency peaks in the Raman spectrum due to acoustic vibrations localized at microscopic particles. The existence of two types of vibrational modes—spherical and torsional—has also been established.

The samples were synthesized through the disproportionation reaction 2GeO →GE + GeO$_2$ in flowing helium at synthesis temperatures T_s ranging from 300 °C to 550 °C. The result was a heterophase film in which Ge crystals were dispersed in the volume of an amorphous dielectric matrix of GeO$_2$. The Ge:GeO$_2$ molar ratio was 1:1. The synthesis conditions made it possible to control the size of the microscopic crystals. The crystalline nature of the particles and their distribution in the matrix were controlled by transmission electron microscopy and electron diffraction.

The Raman spectra were recorded on a Ramanor U-1000 double spectrometer at room temperature in a 90° scattering geometry with the help of the lines at 5145 and 6471 Å from Ar$^+$ and Kr$^+$ lasers.

We first consider the Raman spectra corresponding to scattering by optical phonons for various average sizes ($\bar{d}$) of the microscopic crystals, from 70 to 300 Å (Fig. 1). These spectra differ in the prominence of the low-frequency shoulder, which in-
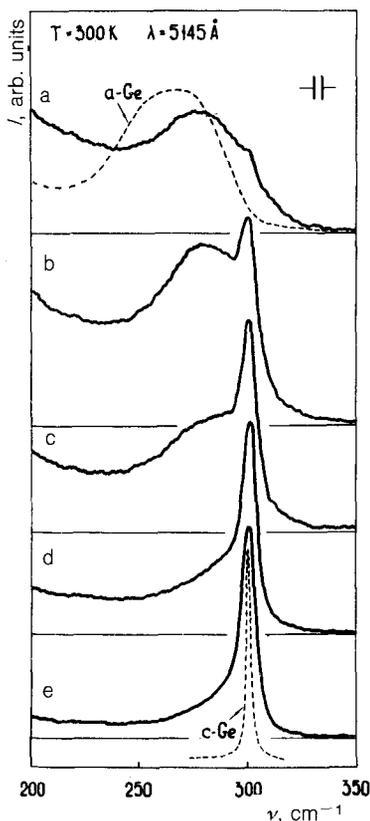

FIG. 1. Spectra of the Raman scattering by optical phonons of Ge microscopic crystals. The parameters are the average size of the microscopic crystals, d, and the synthesis temperature T_s: a—70 Å, 300 °C; b—100 Å, 350 °C; c—150 Å, 400 °C; d—200 Å, 450 °C; e—240 Å, 480 °C. The substrate is sapphire. For comparison, the dashed line shows the Raman spectra of bulk crystalline and amorphous germanium.[9]
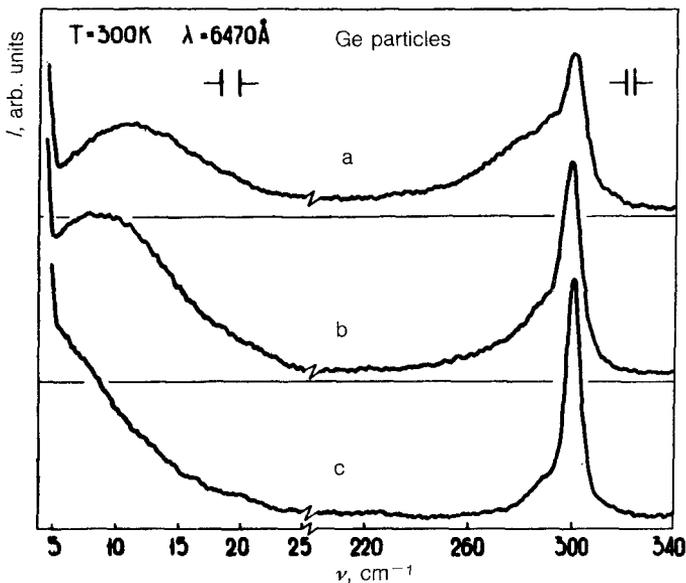
FIG. 2. Spectra of the Raman scattering by natural acoustic vibrations of Ge microscopic crystals and of the scattering by optical phonons of these crystals. d, T_s: a—80 Å, 320 °C; b—110 Å, 360 °C; c—300 Å, 500 °C. The substrate is silicon.

creases with decreasing size of the particles. Similar Raman spectra were observed in Ref. 5 from microscopic crystals of Ge and Si deposited on glass. Hayashi and Abe[5] pointed out that the Raman spectra indicated that the particles on the order of 100 Å in size were amorphous (as in our own case), while high-resolution electron microscopy demonstrated that their structure was crystalline. Accordingly, it is not yet clear just what is primarily responsible for the broadened spectra of the Raman scattering by optical phonons: the surface of the microscopic crystals or their amorphous component.

We turn now to the low-frequency Raman spectra, which are shown in Fig. 2 along with the spectra of the Raman scattering by optical phonons of microscopic crystals. It should be noted that the absorbing Ge particles have an elevated diffuse scattering, so high-quality grating holograms and narrow, stopped-down spectral slits must be used in order to record the low-frequency spectra near the exciting line. It can be seen from Fig. 2 that with decreasing size of the microscopic particles the maximum of the low-frequency peak shifts up the frequency scale. This shift agrees with the expression $\nu \approx v/cd$ for the vibration frequency of small spherical particles,[6] where v is the sound velocity, d is the size of the particle, and c is the velocity of light.

A distinction is made between two types of vibrations of the particles: spherical and torsional. It has been established experimentally[7] that only the low-energy vibrational modes are active in Raman scattering. The observation of these modes requires polarization measurements, since the spherical vibrations lead to a polarized scatter-
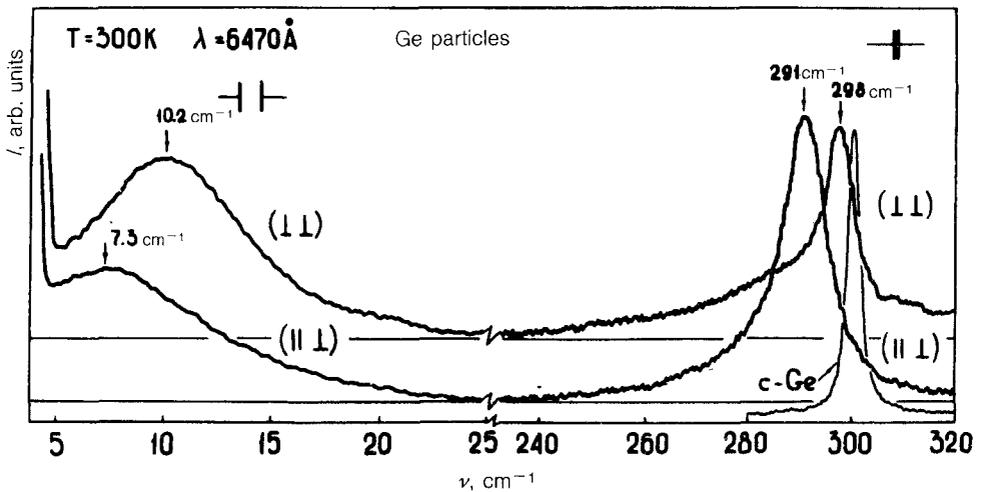
FIG. 3. Polarization dependence of the Raman spectra of Ge single crystals. $d = 130$ Å, $T_s = 380$ °C, fused quartz substrate. Shown for comparison is the spectrum of the Raman scattering by a mixed $LO\text{-}TO$ phonon in crystalline Ge.

ing, while the torsional vibrations lead to a depolarized scattering. The frequencies of these modes at the maximum are $\nu^S_{\max} = 0.7\nu_l/dc$ and $\nu^T_{\max} = 0.85\nu_t/dc$, respectively, where ν_l and ν_t are the longitudinal and transverse sound velocities in the microscopic crystal. Figure 3 shows the Raman spectra of one sample with the different polarizations ($\perp\perp$) and ($\|\perp$), i. e., with the field vector of the exciting wave respectively perpendicular and parallel to the scattering plane, while the scattered wave was perpendicular to the scattering plane in both cases. The maximum of the low-frequency peak in the case of polarized scattering ($\perp\perp$) lies on the high-frequency side of the maximum in the depolarized scattering ($\|\perp$). This result is direct evidence of the existence of two vibration modes in these microscopic crystals. We substitute the experimental values of $\nu_{\max}$ from the spectra of Fig. 3 for the polarized and depolarized scattering into the expressions for the frequencies $\nu^S_{\max}$ and $\nu^T_{\max}$. Their ratio turns out to be $\nu_l/\nu_t = 1.67 \pm 0.01$. On the other hand, the ratio of the sound velocities averaged over the three directions in Ge, $\nu_l = 5.25 \times 10^5$ cm/s and $\nu_t = 3.25 \times 10^5$ cm/s is 1.62. This difference can be tentatively attributed to a deviation of the particles from a spherical shape.

In summary, the low-frequency Raman scattering spectrum carries information about the types of acoustic vibrational modes and the size and shape of the microscopic crystals.

We conclude with a discussion of the shift upon the change in polarization of the spectrum of Raman scattering by optical phonons, shown in Fig. 3. Gaĭsler et al.[8] have established that a surface optical phonon exists near a real Ge surface because of the relaxation of the strength constants of the interatomic interaction. This phonon is associated exclusively with longitudinal vibrations and is shifted about 3 cm^{-1} from

the *LO* bulk phonon. The presence of a thin amorphous layer on the surfaces of the microscopic crystals can be expected to cause a large shift of the surface *LO* phonon at a fixed position of the mixed bulk *LO-TO* phonon. In microscopic crystals, the amplitudes of the contributions of the surface and bulk *LO* phonons to the Raman scattering may be comparable. In this case, however, we should have observed the simultaneous appearance of two peaks for each polarization, since the crystals in the matrix were disoriented, and the system which we studied can be regarded as isotropic on the average. Experimentally, on the other hand, we find only a single peak, at a position which depends on the polarization. It can accordingly be suggested that a mechanism operates to distinguish between *LO* and *TO* phonons on the basis of the polarization in a system of disoriented microscopic crystals. This effect, however, requires further theoretical and experimental study.

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