

Raman scattering by surface vibrations of germanium crystals

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An additional line which has been discovered in the spectrum of the Raman scattering of light by optical phonons in germanium stems from a vibration that is localized near the surface of the crystal. The reasons for the appearance of a vibration of this type are analyzed on the basis of an anharmonicity of optical vibrations. Relaxation of atomic layers near the surface is taken into account.

In this letter we report a study of the Raman scattering of light by optical phonons in germanium which was carried out in order to obtain detailed information on the shape of the Raman scattering line near the $E_1 + \Delta_1$ resonance. Samples of intrinsic Ge were used in the experiments. The surfaces of the samples were subjected to chemical and mechanical polishing and then treated in a polishing etchant. The Raman scattering spectra were excited by lines of Ar^+ and He–Ne lasers and measured with a DFS-52 spectrometer.

Figure 1 shows spectra obtained at $T = 77$ K through the use of various lines of the Ar^+ and He–Ne lasers. The spectra have been scaled to a common peak height. During excitation of the spectrum by a He–Ne laser with $\lambda = 632$ nm, the lineshape has a slight high-frequency asymmetry, which is a consequence of the frequency dependence of the density of two-phonon states.¹ For this excitation wavelength, the effective depth from which the Raman-scattering signal is detected is $(2\alpha)^{-1} = 400$ Å, where α is the absorption coefficient. In the case of the excitation of the spectrum by lines from the Ar^+ laser ($\lambda = 514, 488,$ and 457 nm) the depths to which the light penetrates decreases to 100 Å, and the spectrum reveals a low-frequency asymmetry. For the excitation wavelength $\lambda = 457$ nm, this asymmetry is clearly expressed, taking the form of an additional peak, displaced 2.5 cm^{-1} from the fundamental phonon line of Ge. This new peak, which is shown by the dashed lines in Fig. 1, was found by subtracting from the overall spectrum a symmetric line corresponding to scattering by a bulk phonon.

The experimental results show that the surface state influence the half-width and height of the observed peak (these characteristics may vary by a factor of two or three). The additional peak cannot be due to vibrations of the natural oxide, since the vibrational spectrum of germanium oxide has no frequencies near 300 cm^{-1} (Ref. 2). We believe that the observed peak can be linked with vibrations which are localized near the Ge surface.

Figure 2 shows curves of the intensity of the fundamental and additional lines in the Raman-scattering spectrum of Ge on the excitation wavelength. In contrast with the Raman scattering by the bulk phonon, the cross section for scattering by a surface

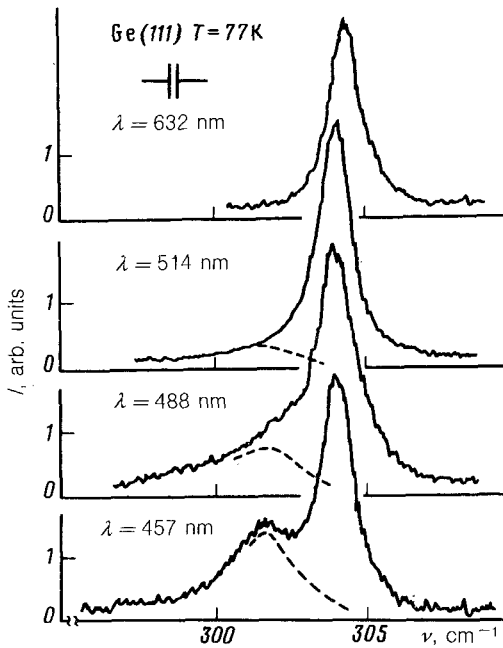


FIG. 1. Spectra of the Raman scattering of light by optical phonons of Ge.

vibration does not undergo a resonant enhancement in the region of the E_1 , $E_1 + \Delta_1$ transitions; this circumstance explains the relative intensification of the additional line with decreasing excitation wavelength (Fig. 1).

Lifshits^{3,4} has derived a theory for the influence of defects (in particular, defects such as a surface) on the vibrational spectra of crystals. The nature of the surface vibration observed here cannot be explained on the basis of that theory, which is based on a harmonic approximation. If we take an anharmonicity of the vibrations into account—in particular, if we allow for a finite phonon lifetime τ —we can formulate

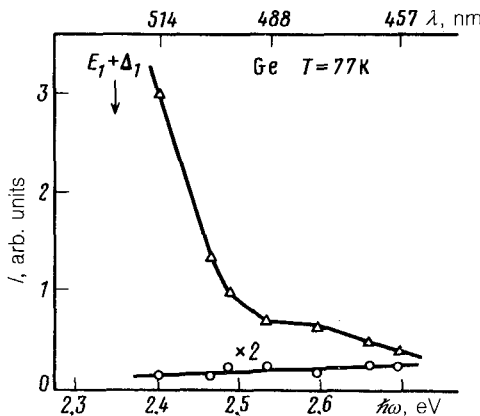


FIG. 2. Intensity of the scattering by bulk (Δ) and surface (\circ) vibrations of Ge versus the excitation wavelengths near the $E_1 + \Delta_1$ transitions.

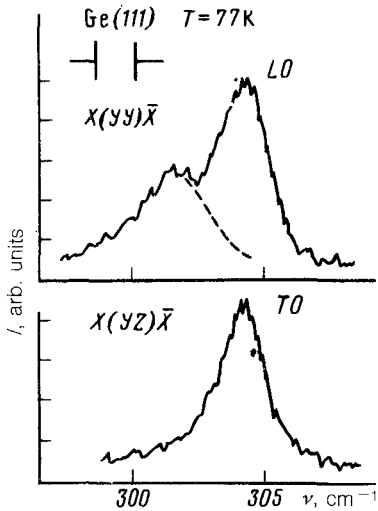


FIG. 3. Raman scattering spectra obtained in various polarization configurations.

reasons for the appearance of a vibration of this type: By analogy with the analysis of thermal conductivity,⁵ where the vibrations of a crystal are treated as spatially localized wave packets, we suggest that the optical vibrations which have a finite lifetime τ and a finite propagation velocity $v(q)$ are localized in a region with a typical dimension $l \cong v(q)\tau$, where $v(q)$ is the group velocity, and q is the position of the center of the packet in wave-vector space. The localization of the vibrations suggests that a defect in the crystal leads to a change in the frequency of these vibrations in a region with a dimension on the order of l . For the optical vibrations of Ge which are detected in the Raman scattering we have $q \cong 5 \times 10^5 \text{ cm}^{-1}$, $v(q) \cong 7 \times 10^3 \text{ cm/s}$, and $\tau \cong 3 \times 10^{11} \text{ s}$. We thus find $l \cong 20 \text{ \AA} = 4a_0$, where a_0 is the lattice constant. A possible change in the strength constants near the surface could thus shift the frequency of the long-wave optical vibration in a region with a dimension $\sim 20 \text{ \AA}$.

To determine the nature of the perturbation of the strength constants of the interatomic interaction near the surface, we carried out polarization measurements of the Raman-scattering spectra; the results are shown in Fig. 3. It follows from the form of the Raman-scattering tensor for Ge that in the case of scattering from the (111) surface in the geometry $X(YY)\bar{X}$ [$X \parallel (111)$], $Y \parallel (1\bar{1}0)$, $Z \parallel (11\bar{2})$ and LO phonon appears in the spectrum, while in the $X(YZ)\bar{X}$ geometry a TO phonon appears.⁶ It can be seen from Fig. 3 that the surface vibration (the dashed line) is of the LO type. This result corresponds to a weakening of the strength constants primarily in the direction perpendicular to the surface. A given perturbation may be associated with either a "cutoff" of the interatomic interaction for the first atomic layer or a relaxation of atomic layers near the surface.

To distinguish between the contribution of the cutoff of the interatomic interaction and that of the relaxational weakening of the constants of the interatomic interaction, we calculated the frequencies of optical vibrations in the model of a one-dimensional chain of eight atoms ($4a_0$). We assumed that the end links of the chain were attached

to two walls. It turned out that a detachment of the first atom from the wall leads to a 0.15% shift of the optical vibration frequency; this shift is substantially smaller than the observed value (1%). In analyzing the effect of relaxation of atomic layers near the surface in this model, we assumed that the strength constants of the interatomic interaction fall off as $(N)^{-2}$ as functions of the link number N . These calculations showed that the frequency of the optical vibration of the chain changes 1% as a result of a relaxation, in the course of which the constant of the coupling between the first and second atoms weakens by 20%. The greatest effect is manifested by a weakening of the central links of the chain; the links nearest the surface have little effect on the vibration frequency. These calculations thus lead to the conclusion that a relaxation of the atomic layers near the surface is the most likely reason for the appearance of the observed surface vibration.

A study of the spectra from a surface without the natural oxide—prepared by cleaving germanium in liquid helium—showed that the position of the additional line is the same as that in spectra obtained from the real surface. This result is confirmed by an analysis of the effect of an oxide in the same one-dimensional model with a frequency of 800 cm^{-1} for the vibrations of the germanium-oxygen bond.² The calculations show that the addition of an oxygen atom to the end atom of the chain causes a 0.2% shift of the frequency of the optical vibration; this figure does not exceed the experimental error.

In summary, this very simple model of the localization of an optical vibration of the crystal furnishes an explanation of the basic features of the surface vibration which has been observed.

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