Condition (10) is quite stringent. For a triangular lattice with central forces between nearest neighbors (a plausible model for rare-gas monolayers on graphite), one has

$$\kappa_T = \kappa\sqrt{3}, \tag{13}$$

and condition (10) is not satisfied, though the difference lies within "theoretical" error. Experimentally, however, the Novaco-McTague effect has been observed for argon on graphite.[12]

A last comment will be made. In charge-density-wave systems, similar distortions have been observed and received a theoretical, though purely numerical, explanation, which does not use coupling with phonons,[5] and is therefore completely different from ours. It would be interesting to compare the two mechanisms.

The author is indebted to C. Marti for many exciting discussions and information.

[1] A. Thomy and X. Duval, J. Chim. Phys. 67, 1101 (1970).

[2] J. A. Venables and P. S. Schabes-Retchkiman, J. Phys. (Paris), Colloq. 38, C4-105 (1977).

[3] S. C. Fain and M. D. Chinn, J. Phys. (Paris), Colloq. 38, C4-99 (1977).

[4] W. L. McMillan, Phys. Rev. B 14, 1496 (1976).

[5] K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. 43, 1839 (1977).

[6] P. G. de Gennes, Solid State Commun. 10, 163 (1968).

[7] M. Luban, D. Mukamel, and S. Shtrikman, Phys. Rev. A 10, 360 (1976).

[8] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. 38, 1286 (1977).

[9] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, London, 1959), Sect. 1, p. 4.

[10] F. C. Franck and J. H. Van Der Merwe, Proc. Roy. Soc. London, Ser. A 198, 205, 216 (1949).

[11] The author is indebted to D. Mukamel for illuminating discussions on the effect of wall crossing.

[12] A. D. Novaco and J. P. McTague, J. Phys. (Paris), Colloq. 10, C4-116 (1977).

Surface Density of Acoustic Phonons in GaAs

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We calculate the surface density of acoustic phonons for GaAs(110) and relate it to the Brillouin elasto-optic cross section. A continuum of surfacelike excitations is found in good agreement with the position and the shape of the surface structure observed in the measured Brillouin spectrum. The role played by the optical absorption coefficient in determining different scattering mechanisms is also discussed.

Brillouin scattering is up to now the only experimental technique which has been successfully employed to detect thermally excited acoustic phonons in metals and semiconductors.[1,2] In the past it has been used in semiconductors in normal incidence.[1] In this case a proper theory has been developed to understand the position and the line shape of the peaks appearing in the experimental spectra and representing bulk phonons.[1,3]

Only recently Sandercock[2] has shown that Brillouin backscattering spectroscopy can be used as a useful technique of high resolution to detect thermal-equilibrium surface acoustic phonons. The measured spectra show, in addition to the usual Rayleigh wave, the existence of a continuum of modes with surface character whose frequencies ω lie between the transverse and longitudinal bulk thresholds. The line shape of this structure appears to be different in metals (optical absorption coefficient $n_2 > 1$) and semiconductors below the absorption edge ($n_2 < 1$): The spectra of the former present a broad shoulder, while the latter show a rather narrow peak located just below the longitudinal threshold.

The nature of the shoulder in the case of metals has been recently explained in terms of scattering from surface ripples,[4] which in turn is proportional to the normal component of the surface density of phonon states (SDPS). This quantity has been computed by Loudon[4] for an isotropic elastic medium and shows good agreement with the experimental spectrum of polycrystalline Al. The SDPS of a metal (tungsten) has been also evaluated independently by the authors[5] in the frequency range of interest, within a microscopic approach,[6] and supports the existence of a continuum of displacements orthogonal to the surface, located between the bulk threshold frequencies and vanishing at the thresholds.[4]

The aim of the present paper is to show that in opaque semiconductors, as GaAs below the optical absorption edge, the peak observed in the Brillouin cross section just below the longitudinal threshold is well accounted for by modes having surface character belonging to the continuous spectrum. We will also show that the nature of these modes is completely different from that of the modes which appear in the metal spectra, because in semiconductors the elasto-optic scattering dominates over the surface-ripple mechanism.

Let us consider a semi-infinite elastic medium in the half-space $x+y<0$ with a (110) face at $x+y=0$. We expand the displacement field in terms of the vibrations of an infinite medium on which translational invariance is not imposed along the direction normal to the surface:

$$\vec{u}^{\,j}(\vec{k}_{\parallel}, \omega, r_{\perp}) = \sum_{\lambda} \exp(ik_{\perp}^{\lambda} r_{\perp}) a^{j}(\vec{k}_{\parallel}, \omega, k_{\perp}^{\lambda}) \vec{v}(\vec{k}_{\parallel}, \omega, k_{\perp}^{\lambda}). \tag{1}$$

The constants a^j are determined by imposing boundary conditions which ensure that there is no stress acting upon the surface.[7] The normal components $k_{\perp}^{\lambda}$ of the wave vector are the solutions of the bulk-wave secular equation when the frequency ω and the parallel components $\vec{k}_{\parallel}$ of the wave vector are fixed. The eigenvector corresponding to each $k_{\perp}^{\lambda}$ is indicated by $\vec{v}(\vec{k}_{\parallel}, \omega, k_{\perp}^{\lambda})$. Because of the lack of translational invariance along $x+y$, the $k_{\perp}^{\lambda}$'s can assume complex values. Among the waves with complex $k_{\perp}^{\lambda}$ only those which in the interior of the crystal give rise to decaying waves have to be retained. In the forbidden of bulk frequencies all the $k_{\perp}^{\lambda}$'s are complex and we recover the usual Rayleigh or the Rayleigh-type waves.[7] However, in the continuous spectrum we obtain displacements which in general are a mixture of solutions with both real and complex $k_{\perp}^{\lambda}$'s. The number of independent solutions, labeled by the branch index j in Eq. (1), equals the number of phonons which are present in the bulk at fixed ω and $\vec{k}_{\parallel}$.[8]

The SDPS written in terms of the displacement field (1) and projected along the α direction is given by

$$\rho_{\alpha}(\vec{k}_{\parallel}, \omega) = \sum_{j} |u_{\alpha}^{j}(\vec{k}_{\parallel}, \omega, 0)|^{2} \rho^{j}(\vec{k}_{\parallel}, \omega), \tag{2}$$

where $\rho^j(\vec{k}_{\parallel}, \omega)$ is the unperturbed bulk density relative to the jth branch. The existing theory of inelastic light scattering by a crystal surface[9] shows that the main features of the scattering cross section in the frequency region between the thresholds are due to the SDPS multiplied by the thermal factor. Therefore in the high-temperature limit we approximate the Brillouin cross section with the SDPS times $k_B T/\hbar\omega$. In the following we include this factor in the SDPS. The error that we are making in approximating the scattering cross section with the SDPS does not alter the position and the character of the surface features, as also supported by numerical evaluations.[9] We would like to point out that the SDPS and the scattering cross section became very different for frequencies well above the longitudinal threshold. In this region the scattering cross section exhibits well-defined peaks, corresponding to bulk phonons,[2] which are totally absent in the SDPS. Furthermore, because the experimental data of GaAs refer to light with wave vector $\vec{k}_{\parallel}$ along $[1\bar{1}0]$ and polarized in the sagittal plane,[2] only the sagittal components of the displacements are to be considered in the evaluation of the cross section.[9]

In the calculations we have used the known values of the elastic constants of GaAs.[7] A sketch of frequency versus $k_{\perp}$ in the complex k plane is given in Fig. 1. The three branches are labeled by their character at the thresholds ω_{x-y} and ω_{x+y}: *sl* and *st* indicate sagittal modes with longitudinal and transverse polarization at ω_{x-y}

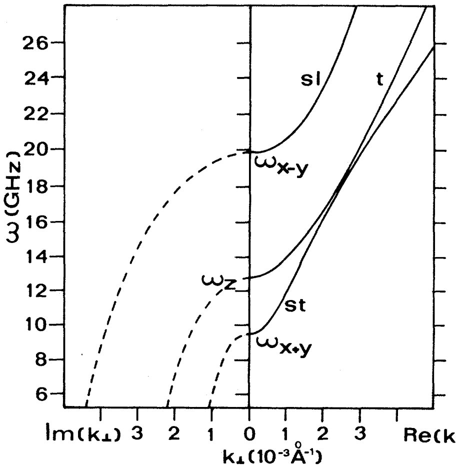

FIG. 1. Dispersion relation $\omega = \omega(\vec{k}_{\parallel}, k_{\perp})$ for GaAs plotted vs complex $k_{\perp}$. $\vec{k}_{\parallel}$ is directed along $[1\bar{1}0]$ on the (110) surface and is the same as in Ref. 2.

and ω_{x+y}, respectively. The z-transverse branch which is orthogonal to the sagittal plane is labeled by t. The stress-free surface equations for the displacement field (1) give rise below ω_{x-y}—where $k_\perp^{sl}$ and $k_\perp^{st}$ are both imaginary—to the usual Rayleigh wave. Surface effects may be also present between ω_{x-y} and ω_{x+y}, where the sagittal-type two-dimensional displacements at the surface are

$$\begin{aligned} u_{x-y}^{\,s} &= a^s(k_\perp^{sl})v_{x-y}(k_\perp^{sl}) + [a^s(k_\perp^{st}) - a^s(-k_\perp^{st})]\,v_{x-y}(k_\perp^{st}), \\ u_{x+y}^{\,s} &= a^s(k_\perp^{sl})v_{x+y}(k_\perp^{sl}) + [a^s(k_\perp^{st}) + a^s(-k_\perp^{st})]\,v_{x+y}(k_\perp^{st}). \end{aligned} \tag{3}$$

In writing Eq. (3) we have used the symmetry properties of the (110) surface. From Fig. 1 and Eqs. (3) it can be seen that for the sagittal modes in this frequency range there are two real wave vectors ($\pm k_\perp^{st}$) and one imaginary ($k_\perp^{sl}$). The displacement $\vec{u}^{\,s}$ represents a wave incident on the surface ($-k_\perp^{st}$), plus a reflected wave ($+k_\perp^{sl}$). The sagittal SDPS $\rho_{x-y}+\rho_{x+y}$ is shown in Fig. 2. The Rayleigh wave is indicated by the heavy vertical line. The most remarkable feature of this calculation is the appearance of a peak just below ω_{x-y}, not present in the bulk density of states projected on the (110) plane. The peak is due to the behavior of $a^s(k_\perp^{sl})$, which is rapidly increasing when $\omega \to \omega_{x-y}$, while $a^s(+k_\perp^{st})$ and $a^s(-k_\perp^{st})$ are much smaller and nearly constant. This structure represents a continuum of excitations having character and localized near the surface. In fact $v_{x-y}(k_\perp^{sl}) \gg v_{x+y}(k_\perp^{sl})$ for $\omega < \omega_{x-y}$ and $k_\perp^{sl}$ is imaginary. Note that at frequencies greater than ω_{x-y} the SDPS shows the one-dimensional divergence $(\omega-\omega_{x-y})^{-1}$. This singularity is washed out in the experimental spectra because of the average produced by the measure, both on the frequency and on the direction of the wave vector of the light. The invariance under inversion of the (110) surface has the consequence of replacing the other singularity $(\omega-\omega_{x+y})^{-1/2}$, present in the projected bulk density of states, with the behavior $(\omega-\omega_{x+y})^{1/2}$. The experimental points in Fig. 2 are those of Sandercock.[2] They compare well with the present calculation. In

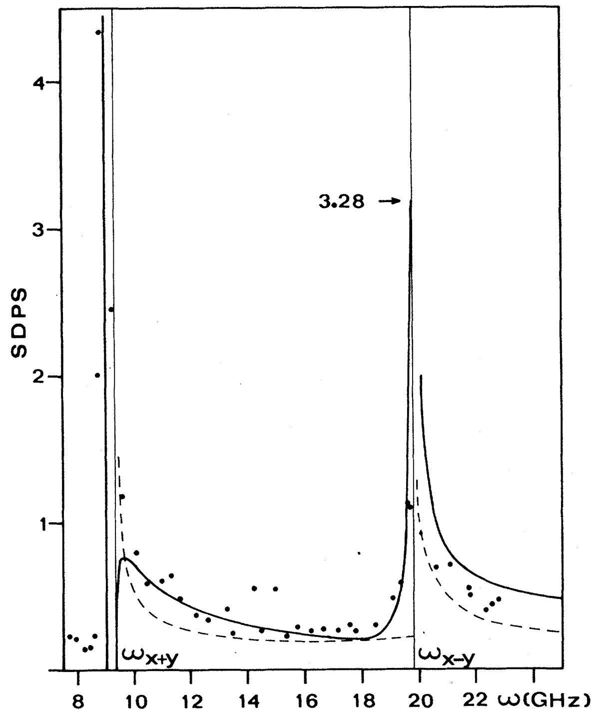

FIG. 2. Full line, SDPS for GaAs multiplied by the thermal factor $k_BT/\hbar\omega$. Dashed line, bulk projected density of states. The experimental points are from Ref. 2.

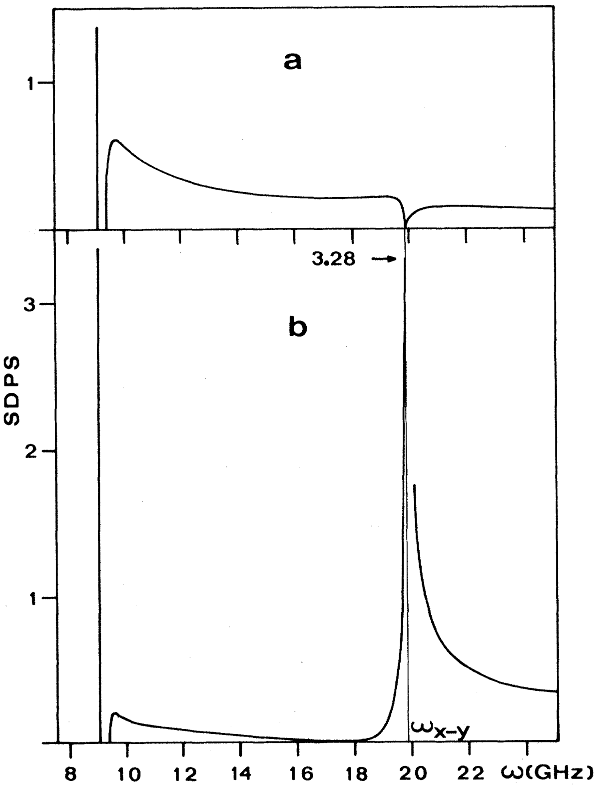

FIG. 3. (a) Transverse-sagittal SDPS ρ_{x+y}. (b) Longitudinal-sagittal SDPS ρ_{x-y}.

particular, the experimental peak located just below ω_{x-y} is explained by the continuum of states we have found below the threshold frequency.

The sagittal SDPS is split, in Fig. 3, into its longitudinal and transverse components. We point out the different behavior of these contributions at the longitudinal threshold, where ρ_{x+y} vanishes but ρ_{x-y} exhibits a maximum. When elasto-optic scattering occurs, as in semiconductors with $n_2 < 1$, both ρ_{x+y} and ρ_{x-y} contribute to the Brillouin spectrum and the most significant structure is the peak in ρ_{x-y}. On the contrary, if $n_2 > 1$ the surface reflection coefficient is large, the ripple mechanism becomes dominant and only the orthogonal projections of the displacements (ρ_{x+y}) contribute to the spectrum.[4] This mechanism should be also observable in GaAs by lowering the wavelength of the incident light.

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[1] J. R. Sandercock, Phys. Rev. Lett. 28, 237 (1972).

[2] J. R. Sandercock, to be published, and private communication.

[3] A. Dervish and R. Loudon, J. Phys. C 9, L669 (1976).

[4] R. Loudon, Phys. Rev. Lett. 40, 581 (1978).

[5] V. Bortolani, F. Nizzoli, G. Santoro, and E. Tosatti, to be published.

[6] V. Bortolani, F. Nizzoli, and G. Santoro, in *Proceedings of the International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1978), p. 302.

[7] G. W. Farnell, in *Physical Acoustic*, edited by W. P. Mason (Academic, New York, 1970), Vol. 6, p. 109.

[8] B. I. Bennett, A. A. Maradudin, and L. R. Swanson, Ann. Phys. (N.Y.) 71, 357 (1972).

[9] T. E. Feuchtwang, Phys. Rev. 155, 731 (1967).

Calculated Bulk Properties of the Actinide Metals

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Self-consistent relativistic calculations of the electronic properties for seven actinides (Ac–Am) have been performed using the linear muffin-tin orbitals method within the atomic-sphere approximation. Exchange and correlation were included in the local spin-density scheme. The theory explains the variation of the atomic volume and the bulk modulus through the $5f$ series in terms of an increasing $5f$ binding up to plutonium followed by a sudden localization (through complete spin polarization) in americium.

The variation of the atomic volume in the actinide series of elements, shown in Fig. 1, was originally accounted for in terms of a valence picture[1,2] where the $5f$ electrons were considered to be nonbonding just as the $4f$ electrons are in the rare-earth metals. However, more recently it has become increasingly clear, both from experimental and theoretical work,[3] that this is not a valid picture of the real behavior exhibited by the $5f$ electrons. Kmetko and Hill[4] made band-structure calculations for the lighter actinides and found that the width of the $5f$ band is comparable to the d-band width of the heavier $3d$ elements. Subsequent extensions of this work,[5]