Disorder-Activated Acoustic Mode in Raman Spectrum of $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$†

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We report the observation of an acoustic phonon mode, usually not Raman active, which is interpreted here as a disorder-activated longitudinal acoustic mode. Because of good matching of lattice constants and nearest-neighbor force constants in the alloy system $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$, a simple theory has been successfully applied to obtain information on the electronic states.

We have studied the Raman scattering of the alloy system $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$.[1] Among the many phonon modes observed, an acoustic phonon mode involving single-phonon processes is of particular interest, because such a mode is usually not Raman active. This mode is interpreted to be one which is activated by electronic wave functions perturbed by the randomness of the crystal field in the alloy. Both the lattice constants and nearest-neighbor force constants of GaAs and AlAs are nearly equal; therefore, the acoustic phonon modes at the zone edge are almost identical for both compounds. These facts allow us to use a simple theory to extract information on the electronic states in the random system $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$.

Most of our experiments were done with a mixed crystal of $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ grown by a modified Bridgman process, having a range of Al from 16 to 100%. The experimental setup consisted of a Spex 1402 double spectrometer, a He-Ne laser, and a photomultiplier arranged in the backscattering geometry.

Figure 1 shows a typical Raman spectrum from a (100) surface of the alloy for $x=0.24$ with the incident and scattered light polarized in $(\parallel, \parallel)$. The spectrum of the disorder-activated longitudinal acoustic (DALA) mode is the longitudinal acoustic mode activated by electronic states perturbed as a result of the disordered crystal field. The modes TO_1 and LO_1 (TO_2 and LO_2) are the transverse and longitudinal optical branches originating from AlAs (GaAs). A localized phonon mode, designated by AL (acoustic local), is due to the motion of As atoms about a Ga atom on an Al site.[2]

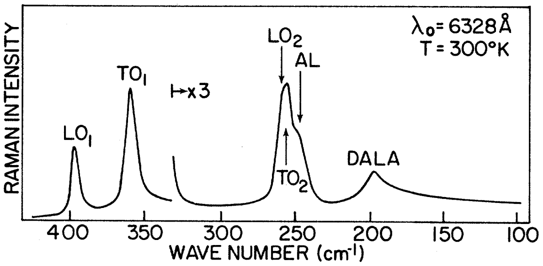

FIG. 1. Typical Raman spectrum for $(\parallel, \parallel)$ backscattering from a (100) surface of $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ for $x=0.24$.

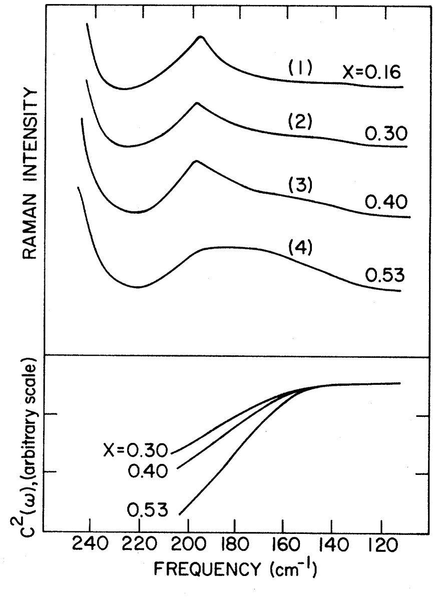

FIG. 2. Top: Raman spectra of disorder-activated longitudinal acoustic modes for various molar fractions x of Ga in the alloy $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$. Bottom: Normalized spatial charge-density fluctuation $|C(\omega)|^2$ obtained as the ratios of curves (2), (3), and (4) to curve (1).

The DALA spectra for various compositions are shown in the upper part of Fig. 2. The polarization dependence for the DALA mode is primarily $(\parallel, \parallel)$ or $(\perp, \perp)$ for a (100) surface with insignificant intensity for cross polarization. It is seen that the peak position has no significant shift, although the general line shape changes with composition. Since the force constant between As and Ga is almost equal to that between As and Al, the frequencies of acoustic phonons at the zone boundary are almost constant throughout the whole range of concentration. The observed peak frequency of 197 cm^{-1} is very close to the L-point longitudinal acoustic frequency of 205 cm^{-1} for GaAs determined by neutron scattering.[3] We may eliminate the possibility of two-phonon processes, because we fail to find any combination of two phonons having a value close to 200 cm^{-1}. This peak gradually deteriorates as the concentration of Ga is increased. This cannot be explained by the deterioration of the phonon mode at zone edge, since the zone-edge mode is well defined even for a 50%-50% alloy.

Disorder-induced Raman scattering due to a random lattice was observed by Smith *et al.*[4] for amorphous material and discussed by Shuker and Gammon.[5] In the case of amorphous materials, the first-order Raman-scattering intensity reflects the phonon density of states. Because of the short correlation length for phonon modes, the conservation-of-momentum condition is relaxed. There have been a number of studies on impurity-induced Raman spectra,[6] especially the recent work reported by Harley, Page, and Walker.[7] In Tl-doped alkali halides, they observed a continuous first-order spectrum, forbidden in the perfect crystal, with the intensity proportional to the phonon density of states. They discussed this on the basis of the violation of translation and inversion symmetries of electronic states due to impurity ions. Nair and Walker[8] observed a first-order spectrum similar to the density of states only at the KBr end of the alloy system $\mathrm{KCl}_{1-x}\mathrm{Br}_x$. In our case the acoustic phonon mode is not degraded by alloying, in contrast to the case of amorphous materials. Furthermore, the line shape changes with composition, showing that it does not simply reflect the density of states alone. Because of the uniqueness of this alloy system, these experimental results are analyzed by a simple mathematical treatment.

We shall discuss first-order Raman scattering based on a model involving perturbed electronic states for an alloy having an appreciable randomness in the crystal field, but a nearly "perfect lattice" as far as phonons are concerned. First-order Raman scattering involves a third-order perturbation process with two intermediate virtual states, a and b.[9] For semiconductors and insulators, a is the state in which an electron is excited from the valence band to the conduction band, absorbing the initial photon, and b is the state in which an excited electron or a hole goes to another state in the same band, emitting or absorbing a phonon. The electron and the hole eventually recombine, emitting a photon. These three transitions can occur in any time order, leading to six related processes which give rise to similar terms. The total scattering probability is given by

$$\frac{1}{\tau}=\frac{2\pi}{\hbar^6}\sum_{q,k_S}\sum_{a,b}\left|\frac{\langle f|H_{ER}|b\rangle\langle b|H_{EL}|a\rangle\langle H_{ER}|i\rangle}{(\omega_a-\omega_i)(\omega_b-\omega_i)}+\cdots\right|^2\delta(\omega_i-\omega-\omega_a), \tag{1}$$

where H_{ER} and H_{EL} are the interaction Hamiltonians for the electron and photon and the electron and phonon, respectively; ω_i, ω_s, and ω are the frequencies of the initial photon, the scattered photon, and the emitted or absorbed phonon, respectively; and $\hbar\omega_a$ and $\hbar\omega_b$ are the energies of the intermediate states. Summation over the photon wave vector $\vec{q}$ includes the whole range of the Brillouin zone, and summation over $\vec{k}_s$ includes only the scattered photon within the solid angle $d\Omega$. Since, in the perfect crystal, momentum is conserved in each process, the overall momentum is conserved; namely, $\vec{k}_i-\vec{k}_s=\pm\vec{q}$, where $\vec{k}_i$, $\vec{k}_s$, and $\vec{q}$ are the wave vectors of the initial photon, scattered photon, and emitted (+) or absorbed (−) phonon, respectively. We can observe these phonon modes only at the zone center in a perfect crystal, because k_i and k_s are of the order of 10^5 cm^{-1} for visible light. However, if the electronic state is perturbed by a lattice disorder, the momentum is no longer conserved in each process, so that the whole acoustic branch may be activated.

When a foreign atom is substituted for a host atom in an otherwise perfect crystal, a one-particle wave function for a randomly substituted alloy may be written as

$$\psi_k(\vec{x})=\sum_{K_n}A_{K_n}\exp[i(\vec{k}+\vec{K}_n)\cdot\vec{x}]+\int g(\vec{k}-\vec{k}')\exp(i\vec{k}'\cdot\vec{x})\,d^3k'=\varphi_k(\vec{x})+R_k(\vec{x}), \tag{2}$$

where $\vec{K}_n$ is any reciprocal lattice vector. The above expression clearly illustrates that our wave function is a linear combination of a Bloch part and a random part. If (7) is substituted into the matrix elements in (1), we have

$$\begin{aligned}\langle a|H_{ER}|i\rangle &\propto \hat{\epsilon}_i\cdot\vec{p}_{cv}\,\delta(\vec{k}_2-\vec{k}_1)+\hat{\epsilon}_i\cdot\int(\vec{k}-\vec{k}_1)g_c^*(\vec{k}_2-\vec{k}_1+\vec{q})q_v(\vec{k})\,d^3k,\\ \langle b|H_{EL}|a\rangle &\propto \omega^{-1/2}\delta(\vec{k}_3-\vec{k}_2-\vec{q})+\omega^{-1/2}\int g_c^*(\vec{k}_3-\vec{k}_2+\vec{k}+\vec{q})g_c(\vec{k})\,d^3k,\\ \langle f|H_{ER}|b\rangle &\propto \hat{\epsilon}_s\cdot\vec{p}_{vc}\,\delta(\vec{k}_3-\vec{k}_1)+\hat{\epsilon}_s\cdot\int(\vec{k}-\vec{k}_1)g_v^*(\vec{k})g_c(\vec{k}_3-\vec{k}_1+\vec{k})\,d^3k,\end{aligned}\tag{3}$$

where ω is the frequency of the phonons; $\hat{\epsilon}_i$ and $\hat{\epsilon}_s$ are the polarizations of the initial and scattered light, respectively; $\vec{p}_{cv}$ is the interband momentum matrix element for the Bloch electrons; and $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$ are the wave vectors of electrons in the valence band and in the first and second virtual states of the conduction band, respectively. The subscripts c and v refer to the conduction and valence bands. In expressions (3), the last terms give rise to momentum-nonconserving processes, while the first give rise to ordinary momentum-conserving processes.

A first-order momentum-nonconserving process arises from any one of three combinations of two of the first terms with one of the last terms of expression (3), only one term from each matrix element being used. Summing up these contributions and integrating with respect to $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$, neglecting the $\vec{k}$ dependence of the denominator in (1), we obtain

$$\omega^{-1/2}\hat{\epsilon}_i\cdot\vec{p}_{cv}\;\hat{\epsilon}_i\cdot[\vec{p}_{cv}C(\vec{q})+\vec{J}(\vec{q})],\tag{4}$$

for the configuration of $\hat{\epsilon}_i=\hat{\epsilon}_s$. Here $C(\vec{q})$ is the Fourier transform of the total charge density arising from the random part of the wave function in the conduction band:

$$C(\vec{q})=\int d^3k_1\int d^3k\,g_c^*(\vec{k}+\vec{q})g_c(\vec{k})=\int d^3k_1\int|R_{ck_1}(\vec{x})|^2e^{i\vec{q}\cdot\vec{x}}d^3x.\tag{5}$$

The second term in the bracket of (4) is the Fourier transform of the interband current density arising from the random part of the wave function, which is given by

$$\begin{aligned}\vec{J}(\vec{q})&=\int d^3k_1\int(\vec{k}-\vec{k}_1)[g_c^*(\vec{k}-\vec{q})g_v(\vec{k})+g_v^*(\vec{k})g_c(\vec{k}+\vec{q})]\,d^3k\\ &=\int d^3k_1\int e^{i\vec{q}\cdot\vec{x}}(1/i)[R_{ck_1}(\vec{x})\,\mathrm{grad}R_{vk_1}^*(\vec{x})-R_{ck_1}^*(\vec{x})\,\mathrm{grad}R_{vk_1}(\vec{x})]\,d^3x\\ &=\int d^3x e^{i\vec{q}\cdot\vec{x}}\int\vec{j}_{k_1}(\vec{x})d^3k_1=\int\vec{J}(\vec{x})e^{i\vec{q}\cdot\vec{x}}d^3x.\end{aligned}\tag{6}$$

It is reasonable to assume that the net current density $\vec{J}(\vec{x})$ of the random part of the wave function is zero since the total current density, including the Bloch part, is zero for the ground state. Furthermore, integrating the square of (4) with respect to $\vec{q}$, putting $\vec{J}(\vec{q})=0$, we have the momentum-nonconserving scattering probability

$$\frac{1}{\tau}\propto\int\frac{|C(\vec{q})|^2}{\omega}d^3q=\int\frac{|C(\omega)|^2D(\omega)}{\omega\,d\omega},\tag{7}$$

where $D(\omega)$ is the phonon density of states and $C(\omega)=C(q(\omega))$, $q=q(\omega)$ being the dispersion relation of the LA phonon. For the process in which holes instead of electrons emit or absorb phonons, we have to take the charge density in the valence band instead of in the conduction band in $C(\vec{q})$. Processes with different time ordering lead to the same expression.

For a dilute alloy, $|C(\omega)|^2$ becomes almost constant. Therefore, the line shape of the disorder-induced phonon mode for a dilute alloy is given simply by $D(\omega)/\omega$, similar to the result obtained by Shuker and Gammon.[5] If we assume that the curve (1) in Fig. 2 for 16% Ga represents $D(\omega)/\omega$, we can get the spatial charge-density fluctuation $|C(\omega)|^2$ for higher concentration as the ratios of curves (2), (3), and (4) to curve (1). Results from this decomposition are plotted in the lower curves of Fig. 2. For higher Ga concentration, it is interesting to note that $C(\omega)^2$ decreases with increasing ω, which is interpreted as a delocalization of the charge density for this very special alloy system. This tendency may even be a rather general result in other disordered systems.

In conclusion, using the unique properties of the $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ alloy system, we have successfully interpreted the observed acoustic phonon modes in terms of the charge-density fluctuation arising from the random part of the wave functions.

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[1] The TO phonon frequency at the Γ point is given by [(force constant of the nearest-neighbor atoms)/(reduced mass)]$^{1/2}$. Using 268 and 361 cm^{-1} for the frequencies of TO phonons at the Γ point of GaAs and AlAs, respectively, we find that the force constant of Al-As differs only by 3% from that of Ga-As.

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Spin-Orbit Splitting in Compositionally Disordered Semiconductors

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Because the optical spectra of substitutional semiconductor alloys are so similar to those of the pure compounds, it is widely believed that the virtual-crystal approximation is accurate, i.e., that fluctuations in the crystal potential are negligible. Investigating the effect of alloying on the spin-orbit splitting, we show that this is not true.

Should substitutional semiconductor alloys, such as Si-Ge, Ga-AlAs, or InSb-As, be considered essentially disordered materials? In fact, recent discussions of disordered semiconductors have been restricted to topologically disordered[1] materials, i.e., glasses and amorphous phases. The reason for this is that, in contrast to glasses and amorphous materials, the optical spectra and electronic behavior of these alloys are so similar to those of the ordered, pure parent compounds[2-5] that no effect due to the compositional disorder has been clearly established prior to this Letter. (However, because of the disparity in mass of the substituted elements, the effect of alloying on phonon modes is quite evident.[6])

The usual way to describe an alloy as if it were ordered is to invoke the virtual-crystal approximation[7] (VCA). The VCA assumes a perfect lattice with compositionally averaged atomic potentials at each lattice site. The resulting band structure is exactly analogous to that of the pure compounds forming the alloy because the assumed crystal potential has no disorder. To the authors' knowledge, no explanation why there should be no local fluctuation of the crystal potential has ever been offered. However, it has been widely assumed that if such deviations from the VCA were important, i.e., if they caused significant mixing of the electronic states found in the ordered crystals, then the band edges and the critical-point features of the optical spectra would be concomitantly broadened. The slight broadening of the critical-point features which is detected in electroreflectance[3,5] may be attributed to macroscopic inhomogeneity in the samples.

Van Vechten and Bergstresser (VV-B) have calculated the variation with alloy composition of the various critical-point features of the optical spectrum for alloys of diamond and zinc-blende semiconductors.[8] That calculation neglected spin-orbit splitting entirely so that comparisons were made with weighted averages of the observed (split) features. It was found that good agreement with experiment could be obtained if it was assumed that the actual variation resulted from two separate effects. First, the variation that would obtain in the VCA was calculated using the dielectric two-band model.[9] Then it was assumed that the actual, spin-orbit–averaged energy of the critical-point feature, $\bar{E}_i(x)$, shifted to lower energy[8,10]—without broadening—by an amount

$$\delta\bar{E}_i(x) = x(1-x)C_{FG}{}^2/A \qquad (1)$$