Resonant Interaction between Hydrogen Vibrational Modes in AlSb:Se

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Vibrational modes and their interactions affect numerous physical processes in condensed-matter systems. In the present work, hydrogen vibrations in Se-doped AlSb were investigated with first-principles calculations. Vibrational frequencies were calculated for the longitudinal, transverse, wag (bending), and stretch modes of the Al-H complex. The Al-H stretch mode interacts with a combination mode involving a wag overtone and transverse fundamental. This resonant interaction yields vibrational states that are linear superpositions of the stretch mode and the combination mode. The spatial extent of such excitations is significantly larger than that of a local vibrational mode.

Vibrational interactions in solids affect a range of physical phenomena, including diffusion, energy transfer, and defect stability. Such interactions determine the channels through which local vibrational modes (LVMs) decay into lattice phonons, a research topic that has attracted significant experimental [1] and theoretical [2] effort. Along with their fundamental importance to solid-state physics, vibrational processes have technological implications. At the Si/SiO_2 interface, under hot-electron excitation, Si-D bonds dissociate at a much lower rate than Si-H bonds [3]. The giant isotope effect was explained by strong coupling of the Si-D wag (bending) mode to lattice phonons, which results in efficient vibrational deexcitation [4]. Beyond semiconductors, interactions involving localized modes influence vibrational and thermodynamic processes in amorphous solids [5], metals [6], and polymers [7].

This Letter addresses a vibrational interaction observed in AlSb doped with Se donors [8]. When AlSb:Se was annealed in hydrogen, electrically neutral donor-H complexes formed. The authors proposed a model in which H attaches to a host Al atom in an "antibonding" configuration (Fig. 1), similar to donor-H complexes in GaAs [9] and Si [10]. The Al-H pairs give rise to a wag-mode fundamental ($0 \rightarrow 1$) and overtones ($0 \rightarrow 2$) that were observed with IR spectroscopy. However, while the Al-D complex had one stretch-mode peak, the Al-H complex showed *two* peaks (Fig. 1).

To explain the unusual splitting of the Al-H stretch mode, it was postulated that the Al-H stretch-mode frequency was nearly resonant with a combination of low-frequency modes [11], similar to a Fermi resonance [12–14]. The anharmonic interaction between the Al-H stretch mode and the "combination mode" would cause the states to hybridize and repel each other. Each state would then contain a stretch-mode component and a combination-mode component. Since the combination mode is nearly IR inactive, the IR absorption intensity provides a measure of each state's stretchlike character. This model was supported by measurements under hydrostatic pressure, which showed an avoided crossing between the two modes [11].

The frequencies of the unperturbed combination mode and stretch mode were estimated to be 1611 and 1613 cm^{-1}, respectively. However, the identity of the combination mode has remained a mystery.

To address this problem, in the present work, first-principles calculations were performed [15] to determine the vibrational frequencies of Al-H complexes in AlSb:S, AlSb:Se, and AlSb:Te. To simulate the local environment of the defect, an $Al_{31}Sb_{35}H_{58}$ cluster was used, where the H atoms terminated dangling bonds at the surface [16]. The minimum Al-Sb distances of the relaxed cluster correspond to a lattice constant of 6.35 Å. One Sb atom was then replaced by a group-VI donor, and an H atom was inserted into the antibonding location. Density functional theory with the Becke three-parameter hybrid functionals [17] was used as the method of calculation. The Los Alamos National Laboratory 2-double-zeta basis set was used; this set assigns Dunning-Huzinaga valence double-zeta functions to H atoms [18] and the Los Alamos effective core potential plus double-zeta basis set to the heavier atoms [19]. The geometry was fully relaxed. Upon
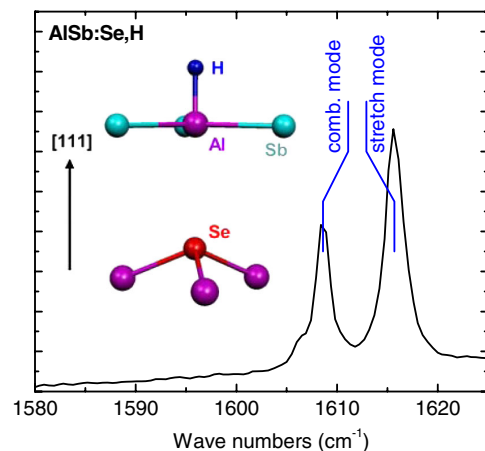

FIG. 1 (color online). Experimental IR spectrum of AlSb:Se,H [8], showing a resonant interaction between the stretch mode and a combination mode.

relaxation, the Al atom moved 1 Å from its substitutional site, along the [111] direction, such that it was nearly coplanar with the 3 Sb atoms (Fig. 1). The calculated Al-H distance was 1.64 Å.

Normal-mode frequencies were calculated within the harmonic approximation from the analytical second derivatives of the energy with respect to the nuclear coordinates. The calculated stretch-mode frequencies were 1665.4 (AlSb:S,H), 1655.0 (AlSb:Se,H), and 1648.5 cm^{-1} (AlSb:Te,H). These values are in reasonable agreement with experimental results for AlSb:Se,H and AlSb:Te,H stretch modes, observed at 1612.9 and 1599.0 cm^{-1}, respectively [8]. The calculated wag-mode frequencies were 640.1 (AlSb:S,H), 641.2 (AlSb:Se,H), and 639.2 cm^{-1} (AlSb:Te,H); i.e., the donor species did not affect the wag mode to within the errors of the calculations [20]. That result is also in agreement with experiment, which measured the AlSb:Se,H and AlSb:Te,H wag modes at 665.7 and 665.0 cm^{-1}, respectively [8]. The insensitivity to donor species arises from the fact that the H atom resides in an antibonding location, well isolated from the donor impurity.

In addition to the stretch and wag modes, the defect had lower-frequency modes that could not be separated from the vibrational modes of the cluster. To isolate the defect modes, all atoms other than the Al-H pair were "frozen" by assigning them masses of 10 000 amu. This approach only altered the stretch and wag modes by a few cm^{-1} (Table I). The lowest-frequency mode at 168 cm^{-1} corresponds to *longitudinal* motion of the Al-H quasimolecule, where the Al and H atoms oscillate in phase along the [111] direction. The next lowest frequency, 269 cm^{-1}, is a doubly degenerate *transverse* mode, involving in-phase motion in the [111] plane. Since both of these modes fall below the spectral range of the IR spectroscopy in Ref. [8], they cannot be compared with experiment directly. The small isotope shifts for the transverse and longitudinal modes are due to the fact that Al and H oscillate in phase such that the mass of the H atom has little effect on the frequency.

For each frequency, the normal-mode displacements and reduced mass (μ) were calculated. To account for anhar-

monic effects, the total energy was calculated numerically as a function of the normal-mode coordinate for the stretch and wag modes. The anharmonic parameters were assumed to be the same for D as for H. For the stretch mode, the calculated energies were fit by a Morse potential [21,22], shown by the solid line in Fig. 2. The fundamental stretch-mode frequency is given by

$$\omega_s = \omega_e - 2\omega_e x_e, \tag{1}$$

where ω_e is the harmonic component and $2\omega_e x_e$ is the anharmonic correction. From the fit, we obtained values of $\omega_e = 1666$ cm^{-1} and $\omega_e x_e = 33.5$ cm^{-1}, resulting in a frequency $\omega_s = 1599$ cm^{-1}.

For the wag mode, the H oscillates in the [111], or *x-y*, plane. Here the origin is centered on the Al-H bond, and the $+y$ axis is defined to point away from one of the three neighboring Sb atoms. The energy was calculated for normal-mode displacements along the x and y directions, denoted Q_x and Q_y, respectively. The potential is given by [23,24]

$$V(x, y) = \tfrac{1}{2}k(Q_x^2 + Q_y^2) + B(Q_x^2 Q_y - Q_y^3/3), \tag{2}$$

where quartic and higher-order terms have been omitted. The parameters k and B were adjusted using the method of least squares, resulting in the solid lines in Fig. 2. The wag-mode frequencies were calculated using second-order perturbation theory (Table II) [25]. The calculated anharmonicity is small, resulting in a split of less than 1 cm^{-1} between the two overtone modes. The anharmonic interaction between the A_1 mode and the stretch mode, neglected in the calculations, would push $\omega_2(A_1)$ downward in frequency. Such an interaction would not affect the E mode. Therefore, we assign the higher frequency to $\omega_2(E)$. This assignment is consistent with the experimental observation that $\omega_2(E)$ is almost exactly twice $\omega_1(E)$.

The calculated frequencies provide an important clue about the identity of the combination mode that interacts resonantly with the Al-H stretch mode. As shown in Table II, the observed mode at 1333 cm^{-1} is assigned to $\omega_2(E)$. The transverse mode also has E symmetry. We propose that *the combination mode is a wag-mode overtone plus a transverse-mode fundamental*. This combina-

TABLE I.   Vibrational modes in AlSb:Se, calculated within the harmonic approximation. The vectors indicate the relative motion of Al and H, where an "up" arrow denotes the [111] direction.

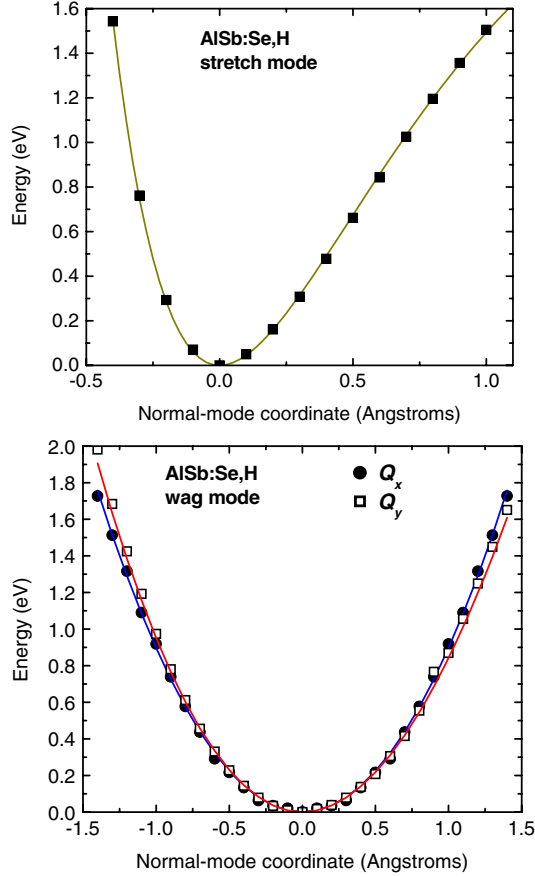| Mode	Al-H frequency (cm^{-1})	Al-D frequency (cm^{-1})	Unit displacement vectors
Stretch (A_1)	1655	1188	↑ ↓
Wag (E)	637	453	→ ←
Transverse (E)	269	268	→ →
Longitudinal (A_1)	168	165	↑ ↑

FIG. 2 (color online).   Total energy of the AlSb:Se,H complex, calculated for displacements of the Al and H atoms along the stretch- and wag-mode coordinates. Solid lines are fits to anharmonic potentials.

tion mode is represented by $E \otimes E = A_1 \oplus A_2 \oplus E$. The A_1 component can interact anharmonically with the stretch mode, which also has A_1 symmetry. The anharmonic term that causes this coupling is given by

$$\delta H \sim [Q_{yt}(Q_x{}^2 - Q_y{}^2) + 2Q_{xt}Q_xQ_y]Q_z, \qquad (3)$$

where Q_{xt} and Q_{yt} are the transverse-mode coordinates and Q_z is the stretch-mode coordinate.

The transverse mode should have a frequency of 278 cm^{-1}, so that the combination mode has the correct frequency $1333 + 278 = 1611$ cm^{-1}. This experimentally inferred value for the transverse mode is close to the calculated frequency of 269 cm^{-1}. Our assignment for the combination mode also explains why the Al-D stretch mode does not split. As shown in Table I, the transverse mode shifts downward by 1 cm^{-1} when D is substituted for H. Hence, the Al-D combination mode should lie at $957 + 277 = 1234$ cm^{-1}, which is far above the Al-D stretch mode (1164 cm^{-1}). Since it is off resonance, the Al-D stretch mode does not interact significantly with the combination mode and therefore does not exhibit any splitting. Other combination modes also do not interact resonantly with the stretch modes.

TABLE II. Calculated stretch and wag modes in AlSb:Se, taking into account anharmonic effects.

Mode		Theory (cm^{-1})	Experiment (cm^{-1})[a]
Al-H stretch	ω_s	1599.1	1608.6, 1615.7
Al-H wag overtones	$\omega_2(E)$	1383.5	1333.0
	$\omega_2(A_1)$	1382.7	1315.8
Al-H wag fundamental	$\omega_1(E)$	691.7	665.7
Al-D stretch	ω_s	1196.4	1173.4
Al-D wag overtones	$\omega_2(E)$	971.2	957.4
	$\omega_2(A_1)$	970.9	948.4
Al-D wag fundamental	$\omega_1(E)$	485.6	478.2

[a]Reference [8].

The resonant interaction between the Al-H stretch mode and the combination mode has a profound effect on the spatial extent of the vibrational excitation. The localization of the combination mode is qualitatively different than that of the stretch mode. Since the stretch (and wag) modes have frequencies above the phonon band, they are localized in real space. The transverse mode, however, lies in the forbidden phonon gap. "Gap modes" are more extended than LVMs and involve the oscillation of many neighboring atoms [22,26,27]. In general, only crystals composed of atoms with different masses (e.g., AlSb or GaP) have a forbidden phonon gap.

To investigate the degree of localization quantitatively, vibrational modes were calculated using a spring-and-mass model. The AlSb:Se crystal was simulated by a 216-atom cell with periodic boundary conditions; the positions of Al and H were obtained from our first-principles calculations. Nearest neighbors interacted via stretching and bending force constants [28,29]. The Al-Sb force constants were
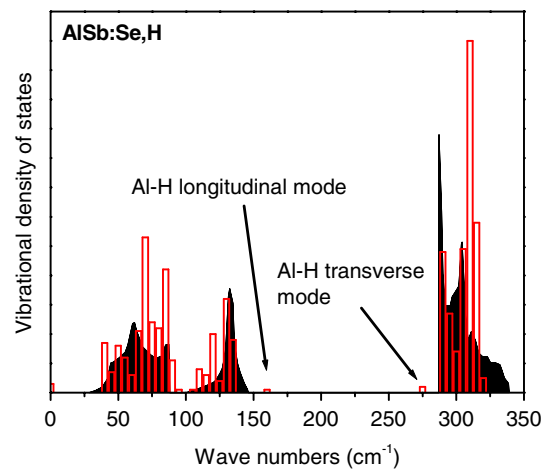

FIG. 3 (color online).   Vibrational density of states versus frequency, calculated using a spring-and-mass model. The height of each bar is proportional to the number of modes. The longitudinal and transverse modes are indicated; the wag and stretch modes are not shown. The black plot is from *ab initio* calculations [30].
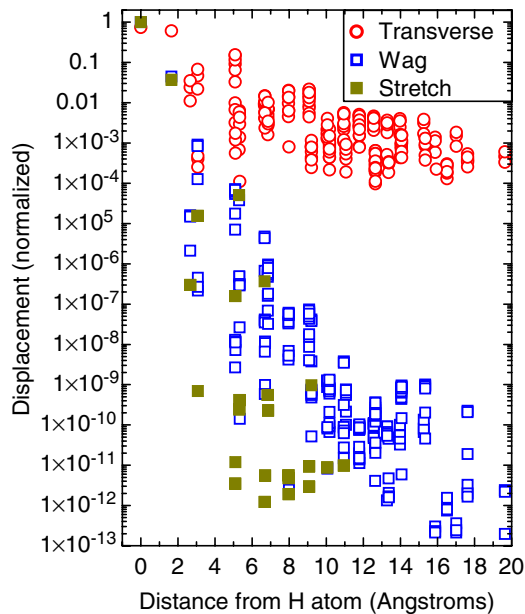
FIG. 4 (color online). Atomic displacement magnitude versus distance from the H atom in AlSb:Se,H, for the transverse, wag, and stretch modes. The transverse mode lies in the forbidden gap and is therefore much less localized than the wag and stretch modes.

adjusted to simulate the AlSb phonon dispersion determined from *ab initio* calculations [30] and neutron scattering experiments [31]. The force constants between the displaced Al atom and its nearest neighbors were adjusted to match the experimental wag and stretch frequencies.

The results of the spring-and-mass model are shown in Figs. 3 and 4. The vibrational density of states (Fig. 3) shows gap modes that correspond to the transverse and longitudinal Al-H modes. Wag and stretch modes, not shown in the figure, were also present. Figure 4 shows the atomic displacements as a function of distance from the H atom. The wag and stretch modes are highly localized, with essentially no atomic motion for distances greater than 10 Å. The transverse mode, in contrast, exhibits atomic displacements *several orders of magnitude greater.*

In conclusion, we identified a candidate for the combination mode that interacts resonantly with the Al-H stretch mode in AlSb:Se. This combination mode, a wag-mode overtone plus a transverse-mode fundamental, has a frequency that is nearly equal to that of the Al-H stretch mode, leading to a resonant interaction. Unlike a Fermi resonance, which involves two local modes, this interaction involves a localized and an extended mode. The spatial extent of the resultant vibrational states is significantly greater than that of an LVM. It is conceivable that such quasiparticles, which exist midway between phonons and localized states, will be discovered in a range of condensed-matter systems.

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[1] B. Sun *et al.*, Phys. Rev. Lett. **96,** 035501 (2006).
[2] D. West and S. K. Estreicher, Phys. Rev. Lett. **96,** 115504 (2006).
[3] J. W. Lyding, K. Hess, and I. C. Kizilyalli, Appl. Phys. Lett. **68,** 2526 (1996).
[4] C. G. Van de Walle and W. B. Jackson, Appl. Phys. Lett. **69,** 2441 (1996).
[5] J. Sarnthein, A. Pasquarello, and R. Car, Science **275,** 1925 (1997).
[6] V. Keppens *et al.*, Nature (London) **395,** 876 (1998).
[7] R. Bruinsma, K. Maki, and J. Wheatley, Phys. Rev. Lett. **57,** 1773 (1986).
[8] M. D. McCluskey *et al.*, Phys. Rev. B **53,** 16 297 (1996).
[9] J. Vetterhöffer *et al.*, Phys. Rev. B **50,** 2708 (1994).
[10] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56,** 769 (1986).
[11] M. D. McCluskey *et al.*, Solid State Commun. **106,** 587 (1998).
[12] E. Fermi, Z. Phys. A **71,** 250 (1931).
[13] G. D. Watkins *et al.*, Phys. Rev. Lett. **64,** 467 (1990).
[14] J.-F. Zheng and M. Stavola, Phys. Rev. Lett. **76,** 1154 (1996).
[15] GAUSSIAN 03, revision A.1, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA, 2003.
[16] See EPAPS Document No. E-PRLTAO-102-089915 for the Gaussian input file. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[17] A. D Becke, J. Chem. Phys. **98,** 5648 (1993).
[18] T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, edited by d. H. F. Schaefer III (Plenum, New York, 1976), Vol. 3, pp. 1–28.
[19] W. R. Wadt and P. J. Hay, J. Chem. Phys. **82,** 284 (1985).
[20] Because of a numerical artifact, the calculated wag-mode frequencies were split by ∼10 cm^{-1}. Frequencies cited for wag modes are the averages of the two values.
[21] P. M. Morse, Phys. Rev. **34,** 57 (1929).
[22] M. D. McCluskey, J. Appl. Phys. **87,** 3593 (2000).
[23] R. C. Newman, Adv. Phys. **18,** 545 (1969).
[24] M. Dean Sciacca *et al.*, Phys. Rev. B **51,** 6971 (1995).
[25] Reference [8] reported other, smaller IR peaks that may correspond to unidentified impurities in the AlSb: Se sample. The peaks labeled as ''fourth harmonics'' in Ref. [8] should actually be assigned to wag overtones.
[26] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. **47,** S1 (1975).
[27] E. G. Grosche *et al.*, Phys. Rev. B **51,** 14 758 (1995).
[28] M. D. Sciacca *et al.*, Phys. Rev. B **53,** 12 878 (1996).
[29] P. N. Keating, Phys. Rev. **145,** 637 (1966).
[30] P. Giannozzi *et al.*, Phys. Rev. B **43,** 7231 (1991).
[31] D. Strauch, B. Dorner, and K. Karch, in *Proceedings of the 3rd International Conference on Phonon Physics*, edited by W. Ludwig, S. Hunklinger, and G. Weiss (World Scientific, Singapore, 1990), p. 82.
[32] C. Catlett *et al.*, in *HPC and Grids in Action*, edited by Lucio Grandinetti, Advances in Parallel Computing (IOS Press, Amsterdam, 2007).