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ANTI-CROSSING BEHAVIOR OF LOCAL VIBRATIONAL MODES IN AlSb

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Using infrared spectroscopy we have observed a resonant interaction between local vibrational modes (LVM's) and unidentified modes in AlSb. This interaction leads to a splitting of the Se–H stretch mode into three peaks at 1606.3, 1608.6 and 1615.7 cm^{-1} at liquid-helium temperatures. As the temperature or pressure is increased, the peaks show anti-crossing behavior. © 1998 Elsevier Science Ltd. All rights reserved

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Resonant interactions between weakly coupled systems play an important role in a variety of phenomena in solid state physics. The study of such interactions has led to discoveries of new quasi-particles such as polarons [1] and polaritons [2]. Thus far most of these studies have been limited to interactions between electronic and vibronic subsystems of the lattice, since small changes in electronic properties can be easily detected and the energy levels may be tuned by external perturbations such as magnetic field or pressure. Recently, Zheng and Stavola [3] have discovered a Fermi resonance between wag and stretch local vibrational modes (LVM's) in donor-hydrogen complexes in silicon. In this letter, we report evidence of a resonant interaction between LVM's and two unidentified modes. By varying the temperature and pressure to change the phonon energies, we have observed anti-crossing behavior between the three modes.

Variable temperature spectra were obtained with a Bomem DA8 spectrometer with a KBr beamsplitter and a mercury cadmium telluride (MCT) detector. Variable pressure spectra were obtained with a Digilab 80-E spectrometer with a KBr beamsplitter and an instrumental resolution of 1 cm^{-1} . To generate hydrostatic pressures up to 15 kbar, we used a modified Merrill-Basset diamond-anvil cell [4, 5]. The liquid immersion-technique [6] was

used to load the cell with liquid nitrogen. A light-concentrating cone focused the light through the diamonds and sample and into a Ge : Cu photoconductor mounted directly behind the sample. We used the pressure dependence of the AlSb : C_{Sb} LVM as a precise *in situ* calibration of the sample pressure [7].

As noted previously [8], at liquid-helium temperatures, hydrogenated AlSb : Se has stretch mode peaks at 1608.6 and 1615.7 cm^{-1} , whereas Se–D mode has only one stretch mode peak at 1173.4 cm^{-1} . In addition, there is a small Se–H peak at 1606.3 cm^{-1} . Hydrogenated and deuterated AlSb : Te have only one stretch mode peak each, at 1599.0 and 1164.4 cm^{-1} respectively. The ratio of the three Se–H peaks is constant from sample to sample, which suggests that they are not due to additional impurity complexes. The details of the crystal growth, sample preparation and hydrogenation techniques are given in [8].

The temperature dependence of the Se–H and Se–D stretch modes is shown in Fig. 1. The linewidth broadening and shift to lower frequency with increasing temperature are seen in numerous semiconductor systems and are caused by an anharmonic interaction between the localized mode and acoustic phonons [9, 10]. As explained by Elliot *et al.* [9], temperature dependent linewidth broadening is primarily due to elastic scattering of acoustic phonons, which results in a dephasing of the local mode. In our case, this temperature dependent broadening causes peaks 0 and 1 to overlap such that they

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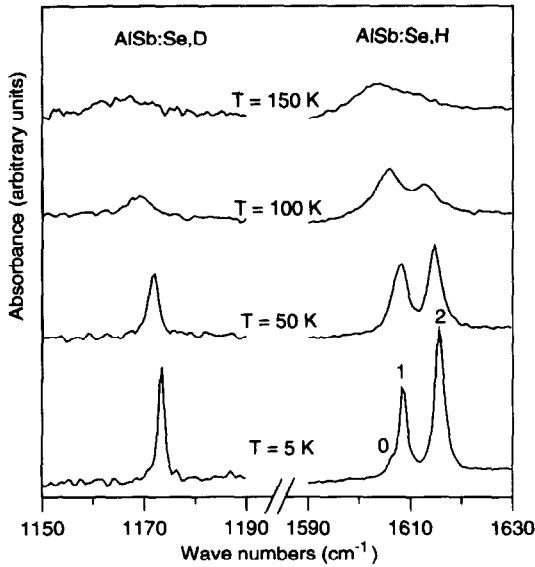


Fig. 1. Temperature dependence of Se–D and Se–H stretch modes in AISb.

are not resolved for temperatures greater than 40 K. For variable temperature measurements, therefore, we refer to the superposition of peaks 0 and 1 as “peak 1”.

The temperature dependent shifts of the local modes are caused by coupling to acoustic phonons and the thermal expansion of the lattice [9]. It has been pointed out, however, that the thermal expansion from 0 to 100 K only results in a shift of $\sim 0.1 \text{ cm}^{-1}$ [10]. In the next few paragraphs the evolution of the Se–H peaks 1 and 2 is discussed. As the temperature increases, the area of peak 1 increases while the area of peak 2 decreases. The sum of the areas remains constant to within the experimental error.

To explain these observations, we propose a model in which the Se–H stretch mode of frequency ω_s interacts with a nearly degenerate mode of frequency ω_1 . The Hamiltonian of this system is given by

$$H = H_s + H_1 + H_{int}, \tag{1}$$

where H_s and H_1 are the Hamiltonians for the two modes and H_{int} is a weak interaction between these systems. Treating H_{int} as a small perturbation, we obtain the following matrix:

$$H = \begin{bmatrix} \omega_s & A \\ A & \omega_1 \end{bmatrix}, \tag{2}$$

where A is an interaction energy. The eigenvalues of this Hamiltonian are given by

$$\omega_{\pm} = \frac{1}{2}[\omega_s + \omega_1 \pm \sqrt{(\omega_s - \omega_1)^2 + 4A^2}]. \tag{3}$$

The corresponding wavefunctions are given by linear combinations of a stretch mode and the unknown mode:

$$|\psi\rangle = a|\text{stretch}\rangle + b|\text{mode1}\rangle. \tag{4}$$

It is assumed that the unknown mode has a negligible absorption coefficient. Given this assumption, the stretch of the absorption peaks are determined solely by the stretch mode contribution to the wavefunction in equation (4), given by

$$|a_{\pm}|^2 = \frac{A^2}{(\omega_s - \omega_{\pm})^2 + A^2}. \tag{5}$$

Experimentally, $|a_{-}|^2$ represents the normalized area of peak 1:

$$|a_{-}|^2 = A_1/(A_1 + A_2), \tag{6}$$

where A_1 and A_2 are the areas of peaks 1 and 2, respectively.

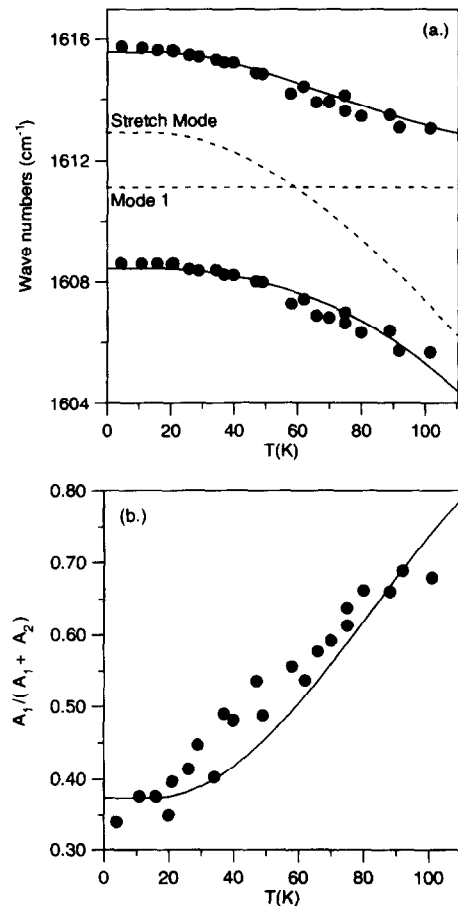


Fig. 2. (a) Se–H stretch mode frequencies as a function of temperature. The dashed lines are the unperturbed stretch mode and “mode 1” [equations (7) and (8)] and the solid lines are the perturbed modes [equation (3)]. (b) Normalized area of Se–H peak 1 (lower-frequency peak). The solid line is a plot of the theoretical model [equation (5)].

In our model, the temperature dependence of the unperturbed stretch mode is given by

$$\omega_s = 1612.9 - 0.034U(T), \quad (7)$$

where $U(T)$ is the mean vibrational energy of the lattice [9, 10] in cal/mole and ω_s is given in cm^{-1} . This temperature dependence is similar to that observed in GaP:Be,H and GaP:Zn,H [10]. The frequency of "mode 1" can be approximated by a constant independent of temperature:

$$\omega_1 = 1611.1 \text{ cm}^{-1}. \quad (8)$$

The parameters in equations (7) and (8) were adjusted to fit the data. As the temperature increases, the area of peak 1 increases as it becomes more "stretch-like" (Fig. 2). Figure 2 shows a comparison between the theoretical calculations and experimental results. The peak frequencies and areas were obtained by fitting to a double Lorentzian function. Using a value of $A = 3.45 \text{ cm}^{-1}$, we can explain the temperature dependence of the peak positions [Fig. 2(a)] as well as the relative absorption strengths of the peaks [Fig. 2(b)].

This model also explains why a splitting in the Se-D mode is not observed. The small interaction energy of $A = 3.45 \text{ cm}^{-1}$ means that a local mode must lie within a few wavenumbers of mode 1 to show an appreciable splitting. The Se-D stretch mode at 1173.4 cm^{-1} is not degenerate with mode 1. The same is true for the Te-H stretch mode at 1599.0 cm^{-1} , which also does not show a splitting.

To further probe the properties of this interaction, hydrostatic pressure was utilized to change the resonance conditions. Varying the pressure has an advantage over

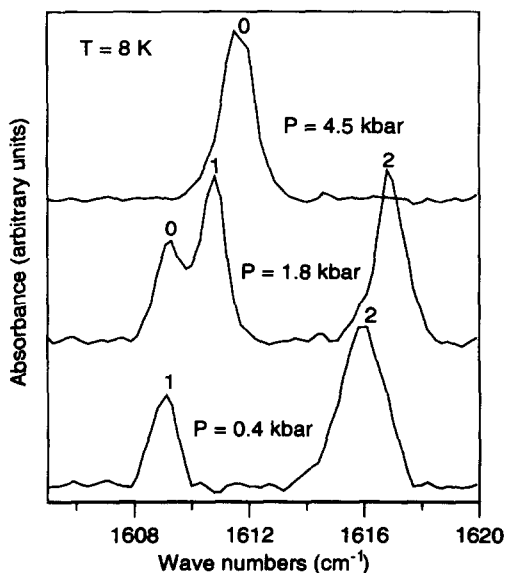


Fig. 3. Se-H stretch mode peaks as a function of pressure.

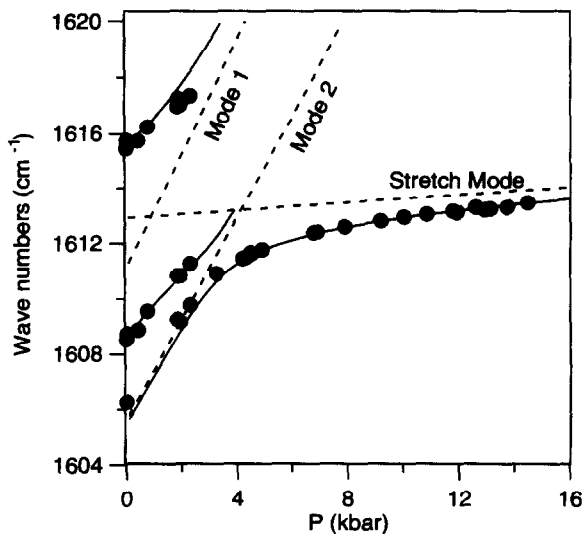


Fig. 4. Se-H stretch mode peaks as a function of pressure. The dashed lines are the unperturbed stretch [equation (11)] and unknown modes [equations (9) and (10)] and the solid lines are plots of the three-level theory [equation (12)].

varying the temperature in that the lines do not broaden, so all three peaks are resolved. We find that the strength of peak 0, which is negligibly small at ambient pressure, increases rapidly at the expense of peaks 1 and 2 (Fig. 3). At pressures above 4.5 kbar, only peak 0 can be detected. The integrated absorption for all the peaks remains constant to within experimental error. The peak positions are plotted in Fig. 4.

To explain the existence of three peaks, we must consider a second mode of frequency ω_2 . The pressure dependence of the peaks can be understood qualitatively as follows: the stretch mode interacts primarily with mode 1 and splits into two branches. The low frequency branch then interacts with mode 2, with a smaller coupling energy. The anti-crossing between the three modes yields three infrared active peaks at pressures of ~ 2 kbar. For higher pressures, only the lowest branch, peak 0, is "stretch-like".

To fit the data, the pressure dependence of the unknown modes are given by:

$$\omega_1 = 1611.1 + 2P \quad (9)$$

$$\omega_2 = 1605.6 + 2P, \quad (10)$$

where P is the pressure in kbar and the frequencies are in units of cm^{-1} . The pressure dependence of the stretch mode is determined by measuring peak 0 at high pressures:

$$\omega_s = 1612.9 + 0.07P. \quad (11)$$

Note that the zero pressure values are the same as those given in the variable temperature analysis.

The three-level Hamiltonian is given by

$$H = \begin{bmatrix} \omega_s & A & B \\ A & \omega_1 & 0 \\ B & 0 & \omega_2 \end{bmatrix}, \quad (12)$$

where A and B are interaction parameters and for simplicity the interaction between the unknown modes is neglected. We use values of $A = 3.45 \text{ cm}^{-1}$, as before and $B = 0.9 \text{ cm}^{-1}$. The eigenvalues of the Hamiltonian [equation (12)] are calculated numerically. We obtain very good agreement between the model and experiment (Fig. 4).

It is unlikely that the observed anti-crossing results from a Fermi resonance between the stretch mode and a wag mode harmonic. From perturbation theory, the $N = 5, \Gamma_1$ wag mode has a predicted frequency of 1665 cm^{-1} [11], which is too far above the stretch mode (1610 cm^{-1}) to strongly interact. In addition, in C_{3v} symmetry there exists only one $N = 5, \Gamma_1$ wag mode, while we observe two unknown modes. These observations suggest that the unknown modes may be combinations of Se-H wag modes and extended lattice phonons. However, we cannot exclude the possibility that the stretch mode resonantly interacts with a local vibrational mode of the Se-H complex that has not yet been discovered.

In conclusion, we have discovered evidence of a resonant interaction between local modes and phonons in AISb. We propose that the Se-H stretch mode interacts with two unidentified modes, resulting in anti-crossing between three distinct peaks.

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REFERENCES

1. Frölich, H., Pelzer, H. and Zienau, S., *Phil. Mag.*, **41**, 1950, 221.
2. Kittel, C., *Quantum Theory of Solids*, John Wiley & Sons, 1987, 34.
3. Zheng, J.-F. and Stavola, M., *Phys. Rev. Lett.*, **76**, 1996, 1154.
4. Merrill, L. and Bassett, W.A., *Rev. Sci. Instr.*, **45**, 1974, 290.
5. Sterer, E., Pasternak, M.P. and Taylor, R.D., *Rev. Sci. Instr.*, **61**, 1990, 1117.
6. Schiferl, D., Cromer, D.T. and Mills, R.L., *High Temp. High Pressures*, **10**, 1978, 493.
7. McCluskey, M.D., Hsu, L., Wang, L. and Haller, E.E., *Phys. Rev.*, **B54**, 1996, 8962.
8. McCluskey, M.D., Haller, E.E., Walukiewicz, W. and Becla, P., *Phys. Rev.*, **B53**, 1996, 16297.
9. Elliot, R.J., Hayes, W., Jones, G.D., MacDonald, H.F. and Sennet, C.T., *Proc. R. Soc. Lond.*, **A289**, 1965, 1.
10. McCluskey, M.D., Haller, E.E., Walker, J. and Johnson, N.M., *Phys. Rev.*, **B52**, 1995, 11859.
11. McCluskey, M.D., Haller, E.E., Walukiewicz, W. and Becla, P., *Mat. Sci. Forum*, **258-63**, 1997, 1247.