LOCALIZED VIBRATIONS OF PHOSPHORUS AND ALUMINUM IMPURITIES IN GaSb

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Reviews of the thoery of localized vibrations of light atomic impurities in crystals have been given recently.¹⁻³ In the case of insulating crystals, experimental investigations have been largely confined so far to the vibrations of H⁻ and D⁻ ions in the alkali halides^{4,5} and the alkaline earth fluorides.⁶ In the case of semiconducting crystals, particular attention has been given to boron impurities in silicon.⁷⁻⁹ Localized vibrations of phosphorus and aluminum impurities in GaSb are described here.

The investigation by infrared methods of localized vibrations of electrically active impurities in semiconductors is made difficult by the associated free-carrier absorption; the free carriers may be removed by counterdoping with other impurities, by electron bombardment, or by a combination of both.⁸ Al impurities in GaSb are expected to replace Ga atoms and P impurities are expected to replace Sb atoms, and since the valence structures are the same in both cases the free-carrier problem does not arise. However, high-purity GaSb has residual acceptors of unknown origin which introduce levels into the crystal with threshold energies at¹⁰ about 250 cm⁻¹ and 500 cm⁻¹; these occur with concentrations of ~10¹⁷/cm³ and compensation of the crystals is essential for the investigation of localized vibrational modes of dilute impurities in the region 300-350 cm⁻¹. Our crystals were grown with both the light impurity and the compensating agent tellurium added to the melt. A spectrochemical analysis of the specimens investigated showed aluminum present at 0.20% molar concentration; the phosphorus concentration could not be determined spectrochemically but is expected to be somewhat less than that of aluminum.

The localized-mode spectrum of phosphorus was measured at room and liquid-nitrogen temperatures (Fig. 1) with a grating monochromator. The background absorption is due to incomplete compensation and to the presence of a GaSb combination band which extends from 320 to 380 cm^{-1} . The spectrum of aluminum at liquid-nitrogen temperature is shown in Fig. 2; in this case compensation is less complete and the



FIG. 1. Absorption coefficient α of the localized vibrational mode of phosphorus impurities in GaSb at (a) liquid nitrogen and (b) room temperature. The left ordinate is associated with curve (a) and the right ordinate with curve (b).



FIG. 2. Absorption coefficient α of the localized vibrational mode of aluminum impurities in GaSB at liquid-nitrogen temperature.

room-temperature curve has not been given because the low transmission of the sample made measurements of α very inaccurate in the vicinity of the peak.

When considering localized modes we shall, as a first approximation, assume the host lattice to be static. The impurity ion vibration is not harmonic and for T_d symmetry (the point symmetry of substitutional sites in GaSb) the potential expanded to fourth order in the displacement of the impurity is⁶

$$V = V_0 + A(x^2 + y^2 + z^2) + B(xyz) + C_1(x^4 + y^4 + z^4) + C_2(x^2y^2 + y^2z^2 + z^2x^2).$$
(1)

The vibrations of the host lattice add terms to (1) coupling localized and band modes.^{6,11} Because of the anharmonic terms in (1), one n=0 $\rightarrow n=2$ and two $n=0 \rightarrow n=3$ overtones of the localized vibrations are allowed and have been observed in the case of H⁻ and D⁻ ions in CaF₂.⁶

The transverse optical (TO) $(\vec{k}=0)$ frequency for GaP occurs at 368 cm⁻¹,¹² for AlSb at 319 cm^{-1} ,¹³ and for GaSb at¹⁴ 230 cm⁻¹; we may compare the localized mode frequencies with these frequencies since an investigation of the lattice combination bands in the case of GaP¹² and AlSb¹³ indicates that the dispersion of the TO frequencies is relatively small. The fact that the fundamental (n = 0 - n = 1) of the localized vibration of phosphorus in GaSb (see Table I) is intermediate between the TO frequency of GaP and GaSb is not surprising since the tetrahedral covalent radius¹⁵ of P (1.10 Å) is less than that of Sb (1.36 Å). However, the tetrahedral covalent radius of Al (1.26 Å) is identical with that of Ga [the lattice constants of AlSb (6.12 Å) and GaSb (6.13 Å) are almost identical. We therefore expect that the localized-mode frequency of Al in GaSb (314 cm⁻¹ at room temperature) should be close to the TO frequency of AlSb (319 cm^{-1}) and the agreement is striking.

Both P and Al have only one stable isotope and in each case only one line is observed. The fundamental $(\Gamma_1 \leftarrow \Gamma_4)$ has a threefold spatial degeneracy in the cubic environment and the sharpness of the localized mode (see Table I) shows that in both cases the cubic symmetry at the impurity site is preserved; in the case of Al at liquid-nitrogen temperature the linewidth is limited by the slit width (2 cm⁻¹). Localized vibrations of lithium impurities in GaAs have also been investigated.¹⁶ Association of the Li impurities with other lattice defects occurs and the degeneracy of the fundamental is raised; in this case the localized-mode spectrum gives detailed information about point-defect configurations in the crystal.

A search in the vicinity of 650 cm⁻¹ for the $n = 0 \leftrightarrow n = 2$ overtone of the phosphorus vibration was unsuccessful and indicated that the value of α for this transition was at least a factor of 30 less than that of the fundamental. The observed ratio of the values of α for these transitions in the case of H⁻ in CaF₂⁶ was ~1/25; the n=0 $\leftrightarrow n=2$ transition is allowed because of anharmonicity and the intensity relative to the fundamental is expected to be smaller in the present case because of smaller vibration amplitudes.

The linewidth of the localized modes is expected to increase with temperature because of the scattering of band modes off the defect.^{6,11} The coupling of the localized and lattice modes also gives rise to a shift in peak position of the lines with temperature.⁶ The change with temperature of the peak positions and widths of the lines should be comparable,¹⁷ and this is found to be so in the present case (see Table I). Very little change in the integrated absorption $\int \alpha(\nu) d\nu$ of the localized mode should occur with change in temperature and we find this to be the case with phosphorus within the precision of our measurements. A detailed discussion of the effects of temperature on the peak position, width, and intensity of localized vibrational modes is in course of preparation.18

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Table I. Parameters of the localized mode spectra of P and Al impurities in GaSb.

	Phosphorus		Aluminum	
Temperature	Peak positon	Linewidth	Peak position	Linewidth
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
Liquid nitrogen	324.0 ± 0.3	2.0	316.7 ± 0.3	<2.0
Room	321.4 ± 0.5	3.6	313.8 ± 0.5	•••

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¹A. A. Maradudin, E. W. Montroll, and C. H. Weiss, Solid State Phys. Suppl. 3 (1963).

²W. Ludwig, Ergeb. Exakt. Naturw. <u>35</u>, 1 (1964).

³R. J. Elliott, Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963 (to be published).

⁴G. Schafer, J. Phys. Chem. Solids <u>12</u>, 233 (1960). ⁵B. Fritz, J. Phys. Chem. Solids 23, 375 (1962).

⁶W. Hayes, G. D. Jones, R. J. Elliott, and C. T. Sennett, Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963 (to be published).

⁷P. G. Dawber and R. J. Elliott, Proc. Phys. Soc. <u>81</u>, 453 (1963).

⁶S. D. Smith and J. F. Angress, Phys. Letters <u>6</u>, 131 (1963).

⁹M. Balkanski and W. Nazarewicz, J. Phys. Chem.

Solids 25, 437 (1964).

- $^{10}\mathrm{E.}$ J. Johnson, thesis, Purdue University, 1964 (unpublished).
- ¹¹E. Hanamura and T. Inui, J. Phys. Soc. Japan <u>18</u>, 690 (1963).

¹²D. A. Kleinman and W. G. Spitzer, Phys. Rev. <u>118</u>, 110 (1960).

¹³W. J. Turner and W. E. Reese, Phys. Rev. <u>127</u>, 126 (1962).

¹⁴M. Haas and B. W. Henvis, J. Phys. Chem. Solids
<u>23</u>, 1099 (1962).
¹⁵L. C. Pauling, <u>The Nature of the Chemical Bond and</u>

¹⁵L. C. Pauling, <u>The Nature of the Chemical Bond and</u> the Structure of Molecules and Crystals (Cornell University Press, Ithaca, New York, 1960), 3rd ed.,

p. 246.

 $^{16}\mathrm{W}.$ Hayes, to be published.

¹⁷W. M. Visscher, Phys. Rev. 134, A965 (1964).

¹⁸R. J. Elliott, W. Hayes, G. D. Jones, H. M. Mac-Donald, and C. T. Sennett, to be published.

EVIDENCE FOR A $T = 2 \Sigma \pi$ RESONANCE

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Since the discovery of the $Y_1^*(1385)$, there has been continuous speculation concerning the existence of a pion-hyperon resonance with isospin T=2, but experiments to date have failed to find any evidence for its existence.^{1,2} To further this investigation, we studied the reaction

$$K^{-} + n(\mathbf{C}) \rightarrow \Sigma^{-} + \pi^{-} + \pi^{+} + \text{recoils} \tag{1}$$

in a 1.15-BeV/c K^- interaction on neutrons in carbon in the Berkeley 30-in. propane chamber. The reaction

$$K^- + n(\mathbf{C}) \rightarrow \Sigma^+ + \pi^- + \pi^- + \text{recoils}$$
(2)

does not give any information concerning any T = 2 resonance, but has been studied for completeness. We also studied the reaction

$$K^{-} + p(\mathbf{C}) \rightarrow \Lambda + \pi^{-} + \pi^{+} + \text{recoils}$$
(3)

to see how a well-known resonance is produced in carbon.

For the charged pionic decays, the scan-table identification of sigmas depended completely on the ionization change at the decay point. This criterion did not bias against higher momentum sigmas,³ but did give a bias against events where the pion track from the sigma decay was steep in the chamber. A total of 330 events of the type (1) was found in our scanning. The lifetime measured for Σ^- from the events $[(1.12 \pm 0.20) \times 10^{-10}]$

sec] agrees with the accepted value.

The pion tracks involved in this experiment were generally long, and the momenta were determined by curvature measurements to approximately 12% on the average. However, the average sigma track length was 1.1 cm, and only a minimum value of the momentum could be obtained from range measurements. The angle of decay and the pion momentum were used to calculate the momentum of the sigma at the decay point. About half of the time, this resulted in solutions that were double-valued corresponding to forward or backward decay of the sigma in the center-of-mass (c.m.) system. For most of these events, ionization of the sigma was used to resolve this ambiguity. For the few cases where the ambiguity was not resolved by sigma ionization, the two solutions were equal within the errors, and the average value was used. The range-momentum relationship was then used to find the sigma momentum at the production vertex, but no constraints were applied at this point.

To observe resonances in the invariant-mass plot, we needed to know the phase space involved. Since, in our case, we had a variable c.m. energy available due to the Fermi momentum of the nucleons in the carbon nucleus, we adopted the following procedure to calculate the phase space: