Lawrence Berkeley National Laboratory
Recent Work

Title
RESONANT RAMAN SCATTERING IN SbSI NEAR THE ABSORPTION EDGE

Permalink
https://escholarship.org/uc/item/6s0599gc

Author
Amer, N.

Publication Date
1975-07-01

eScholarship.org Powered by the California Digital Library
University of California

0 0 0 0 4 3 0 3 1 5 9

Presented at the Proceedings of III
International Conference on Light
Scattering in Solids, Campinaas, Brazil,
July 1975

LBL-3779
c.1

RESONANT RAMAN SCATTERING IN SbSI NEAR THE ABSORPTION EDGE

N. Amer, P. Y. Yu, Y. Petroff, and Y. R. Shen

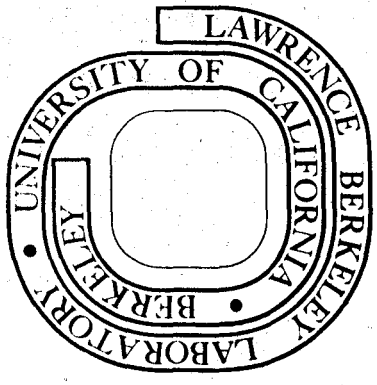
RECEIVED
LAWRENCE
LABORATORY
MAR 24 1978
LIBRARY AND
DOCUMENTS SECTION

July 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-3779
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

To be published in the Proceedings of IIIrd International Conference on Light Scattering in Solids, Campinaas, Brazil, (July, 1975).

LBL-3779

RESONANT RAMAN SCATTERING IN SbSI NEAR THE ABSORPTION EDGE*

N. Amer, P. Y. Yu†, Y. Petroff‡ and Y. R. Shen

Department of Physics, University of California and
Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
Berkeley, CA 94720

ABSTRACT

Resonant Raman scattering in SbSI has been studied in the photon energy region of 1.9-2.3 eV region in both the paraelectric and ferroelectric phases. In both phases a single resonance peak in the Raman cross-section was found for all the observed Raman modes at the absorption edge. The lineshape of the resonance peak was explained satisfactorily by a simple two-band model. Our result suggests that the fundamental absorption edge of SbSI is due to a direct transition.

SbSI is a semiconductor which undergoes a ferroelectric phase transition around room temperature ($T_c \sim 288°K$). There has been considerable interest in its optical[1,2,3] and lattice vibrational properties[4] and their relationship to this phase transition. In this paper we have studied resonant Raman scattering in SbSI at its absorption edge both in the paraelectric and ferroelectric phases. Our purpose is (i) to obtain information on the electron-phonon interaction for the different phonons of SbSI and (ii) to determine if phonons are involved in the absorption edge, i.e. whether the absorption edge is direct or indirect.

EXPERIMENTAL

The SbSI crystals used were needle-shaped, typically 10 x 1 x 2 mm^3 in dimension. The long axis of the needle is parallel to the c-axis. The crystal surfaces were used as-grown without further treatment. The Raman spectra were obtained in four backscattering configurations: $\hat{E}_i \| \hat{E}_s \perp c$, $\hat{E}_i \| \hat{E}_s \| c$, $\hat{E}_i \perp c \| \hat{E}_s$ and $\hat{E}_i \| c \perp \hat{E}_s$ ($\hat{E}_i$ and $\hat{E}_s$ are the polarisations of the incident and scattered radiation respectively). The Raman spectra were excited by the

---

* Research sponsored by Energy Research and Development Administration.

† Present Address: IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598

‡ On leave from University of Paris, Paris IV.

output of a CW dye laser pumped by an Ar^+ laser. By using the dyes: Rhodamine B, Rhodhamine 6G (dissolved in methanol or hexafluoroisopropanol) the dye laser frequency can be tuned continuously from $\sim 15400\ cm^{-1}$ (6500 Å) to $\sim 18200\ cm^{-1}$ (5500 Å). The discrete lines of the Ar^+ laser were used below 5500 Å.

RESULTS

The off-resonance Raman spectra of SbSI we measured at the different temperatures are very similar to those published in the literature[4] so they will not be reproduced here. In the resonant regime the intensities of all the Raman lines change essentially en bloc so the overall shape of the Raman spectra of SbSI is unchanged. As a result in this paper we will show only the dispersion in the Raman cross-section of the strongest mode in each scattering configuration. This is shown in Fig. 1 for the 147°K result. All the curves in Figure 1 show a single peak riding on an increasing background. The position of these peaks agrees well with the on-set of the absorption edge. In Figure 2 we show the enhancement of the 112 cm^{-1} mode ($\hat{E}_i||\hat{E}_s^{\perp}c$) for several different temperatures, both above and below the phase transition temperature. We also measured the resonance in the soft mode slightly below the transition temperature (T = 273°K). We found that the enhancement in the soft mode is only slightly stronger than the other modes.

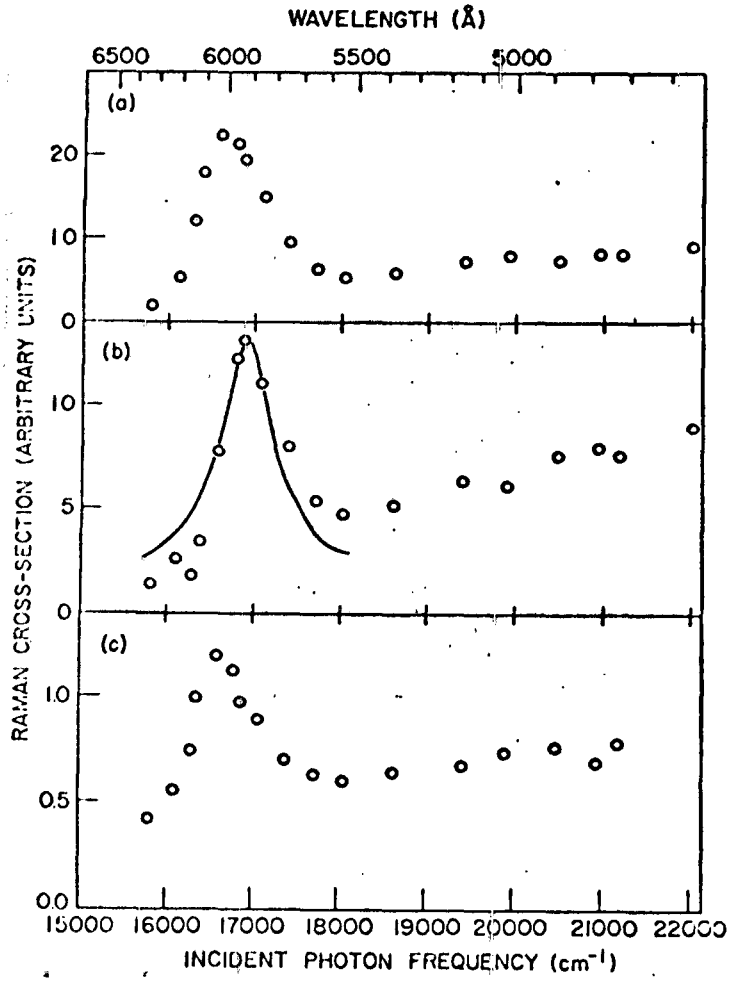


Fig. 1. Dependence of Raman cross-section of SbSI on incident photon frequency obtained at 147°K for 3 different scattering configurations: (a) $\hat{E}_i||\hat{E}_s||c$ (53 cm^{-1} mode); (b) $\hat{E}_i||\hat{E}_s^{\perp}c$ (112 cm^{-1} mode) and (c) $\hat{E}_i||c^{\perp}\hat{E}_s$ (53 cm^{-1} mode). The solid curve in (b) is obtained from Eq. (2) with Γ = 250 cm^{-1}. The peak height and position of the theoretical curve have been normalised to the experimental result.

0 0 0 0 4 3 0 3 1 6 2

There has been some controversy in the literature as to the nature of the fundamental absorption edge in SbSI. Kamimura et al.[2] and Zeinally et al.[2] have analysed the absorption edge of SbSI with the Urbach rule and concluded that the absorption edge is due to a direct transition broadened by the strong interaction between the electron and the 210 cm^{-1} phonon. On the other hand Gerzanich[3] found that the absorption edge is indirect

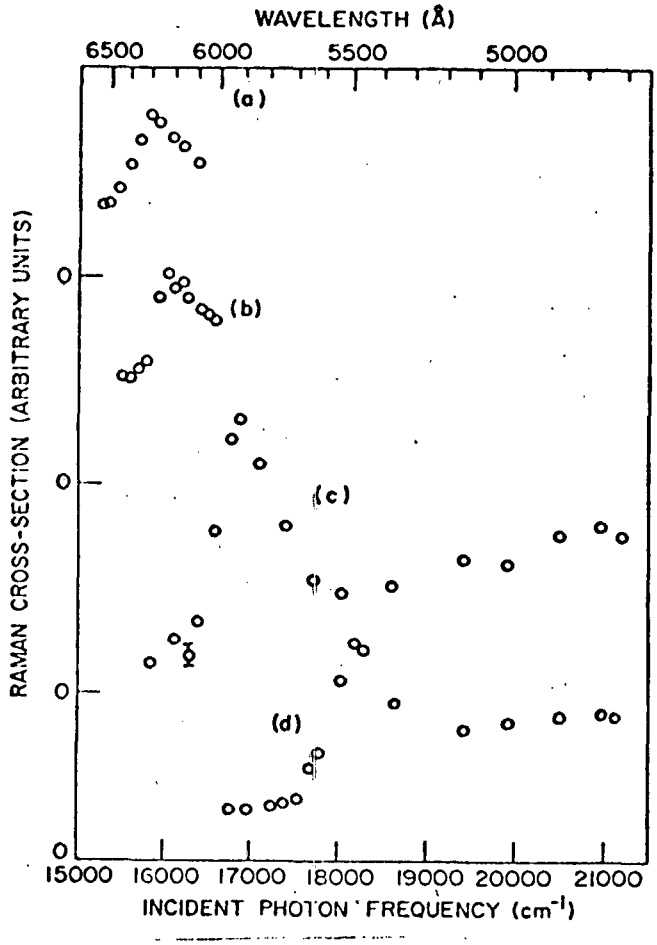


Fig. 2. Dispersion in the cross-section of the 112 cm^{-1} Raman mode measured in the $\hat{E}_i || \hat{E}_s \perp c$ configuration at four different temperatures (a) 291°K (paraelectric phase); (b) 273°K, (c) 147°K and (d) 2°K.

Resonant Raman scattering has been studied in a number of indirect band gap semiconductors (e.g. Si[5], GaP[5], Se[6] and AlAs[5]) and also in a direct but dipole forbidden band gap semiconductor (Cu_2O[7]). It was found in all these semiconductors either there was no enhancement in the Raman cross-section at the indirect gap (such as GaP and Se) or else only two-phonon Raman modes were enhanced. In the latter case (e.g. in Cu_2O and Si) the enhanced mode is usually the overtone of the phonon participating in the absorption process. In SbSI we found that all the observed modes, including one phonon modes were enhanced at the absorption edge. Thus our result suggests that the absorption edge of SbSI is due to a direct transition. However there is a possibility of an indirect gap nearly degenerate with the direct gap but not contributing to resonant Raman scattering (as in Se).

If the electrons at the fundamental gap indeed interact more strongly with the 210 cm^{-1} phonon than the other phonon modes as suggested by Kamimura et al. and Zeinally et al.[2]

we would expect a stronger enhancement in the Raman cross-section of the 210 cm^{-1} mode. Instead we found all the stronger modes (e.g. the 53 cm^{-1}, 112 cm^{-1} modes shown in Fig. 1) were enhanced by approximately the same amount as the 208 cm^{-1} mode. The frequency 210 cm^{-1} obtained from the Urbach rule probably represents an average phonon frequency as seen by the electrons.

Agrawal and Perry[4] tried to fit their resonant Raman result in SbSI (measured by temperature tuning the energy gap) with the Loudon formula for a simple two parabolic band model[8]:

$$R(\omega_i) \propto \begin{cases} (\omega_g-\omega_i)^{1/2} - (\omega_g-\omega_i+\omega_{ph})^{1/2} & \omega_g > \omega_i \\ 0 & \text{otherwise} \end{cases} \qquad (1)$$

when R is the Raman tensor and $\hbar\omega_i$, $\hbar\omega_g$ and $\hbar\omega_{ph}$ are respectively the energies of the incident photon, band gap and phonon scattered. It was pointed out by Martin[9] that Eq. (1) was correct only for $\omega_i < \omega_g$ since it neglected the contribution to R due to the imaginary part of the dielectric tensor when $\omega_i > \omega_g$. According to Martin and Falicov[10] the Raman tensor for the two-band model (including damping) is given by:

$$R(\omega_i) \propto (\omega_g-\omega_i+i\Gamma)^{1/2} - (\omega_g+\omega_{ph}-\omega_i+i\Gamma)^{1/2} \qquad (2)$$

where Γ is a phenomenological damping parameter. In Figure 1 we show a fit to the experimental Raman cross-section using the theoretical expression calculated from Eq. (2). Γ was treated as adjustable and was found to be $\sim$ 250 cm^{-1}. Since Γ is larger than the phonon energy we obtain a single peak instead of two (one at ω_g and one at $\omega_g + \omega_{ph}$ if Γ were smaller than ω_{ph}).

We have also found no significant difference in the resonant Raman behavior of SbSI in the two phases. This is consistent with the fact that the shape of the absorption edge in the two phases are similar and with recent calculations[11] indicating that there is little difference in the overall band structure of SbSI in the two phases.

In conclusion we have studied resonant Raman scattering in SbSI in both the paraelectric and ferroelectric phase. Our result suggests that the fundamental absorption edge of SbSI is direct and most of its phonon modes interact equally strong with the band edge electrons.

REFERENCES

1. C. Harbeke, J. Phys. Chem. Solids 24, 9457 1963); R. Kern, J. Phys. Chem. Solids 23, 249 (1962).

0 0 0 0 4 3 0 3 1 6 4

2. H. Kamimura, S. M. Shapiro, and M. Balkanski, Phys. Lett. 33A, 277 (1970); A. Kh. Zeinally, A. M. Mamedov and Sh. M. Efendiev, Soviet Phys. Semiconductors 7, 271 (1973).

3. E. I. Gerzanich, Soviet Phys.-Solid State 9, 2358 (1968).

4. See "Light Scattering in Solids", M. Balkanski, Flammarion, Paris, France (1971), p. 392-401.

5. P. B. Klein, H. Masui, J. J. Song and R. K. Chang, Solid State Comm. 14, 1163 (1974); P. B. Klein, Thesis, Yale University, (1975) (unpublished); P. Y. Yu (unpublished).

6. P. Y. Yu, N. Amer, Y. Petroff and Y. R. Shen (unpublished).

7. P. Y. Yu, Y. Petroff, Y. R. Shen and L. M. Falicov, Phys. Rev. Lett. 30, 283 (1973).

8. R. Loudon, Proc. Roy. Soc. A275, 218 (1963); J. Phys. Radium 26, 677 (1965).

9. R. M. Martin, Phys. Rev. B10, 2620 (1974).

10. R. M. Martin and L. M. Falicov (unpublished).

11. K. Nako and M. Balkanski, Phys. Rev. 8, 5759 (1973).

0 0 0 4 3 0 3 1 6 5

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720