PROC, 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980 J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 669–672

> SECOND ORDER RAMAN SCATTERING IN MONOCLINIC AND TRIGONAL SELENIUM*

> > P. J. Carroll and J. S. Lannin

Department of Physics The Pennsylvania State University University Park, Pennsylvania 16802 USA

Second order Raman scattering measurements in monoclinic and trigonal Se indicate differences in the phonon density of states for high frequency optic modes. The increased frequency and band shape changes in monoclinic Se arise from the absence of interchain coupling present in trigonal Se. The existence of a peak in monoclinic Se at 220 cm⁻¹ is consistent with weak ring-like excitations in amorphous Se, whose primary spectrum is related to trigonal Se.

I. Introduction

Of basic interest to the lattice dynamics of two-fold coordinated solids, which include Te, Se and S, is the relative role of interunit versus intraunit bonding, where unit refers to either rings or chains. In amorphous Se and Te, for example, it has been suggested that an increase of the high frequency phonon states relative to the trigonal, chain associated phase is a consequence of weakened interchain coupling and corresponding increased intrachain bonding [1,2]. Similarly for ring associated crystalline Se and S materials it has been suggested that the dominant bonding is within rings, given the large inter-ring distances, which imply molecular systems with van der Waal coupling. In this study a comparison of the phonon spectra of monoclinic (m-) and trigonal (t-) Se is made using second order Raman scattering as a probe of the one phonon spectrum. This relation between the second order spectra and the one phonon density of states is possible under conditions of predominant overtone scattering and weak frequency dependent coupling parameters for the bands of interest. For elemental group IV and V semiconductors these conditions have been observed to be essentially satisfied [3,4]. A recent second order study in Te also suggests these conditions hold for high frequency optic modes of interest here [5].

While m-Se has not been previously studied using second order Raman scattering, earlier work on t-Se interpreted the spectra in terms of 2k = 0 processes [6], in contrast to the present analysis. Recent time of flight neutron scattering measurements [7] in polycrystalline t-Se are shown below to imply the present overtone analysis. Furthermore, the higher resolution Raman spectrum indicates additional structure in the phonon spectrum of t-Se at high frequencies not observed in neutron studies. A comparison of the corresponding m-Se spectra is shown to indicate differences in the vibrational spectra of the chain and ring derived Se phases which are also relevant to the structure of amorphous (a-) Se. In particular the spectra are consistent with the predominance of chains in a-Se [8,9].

II. Experiment

Raman scattering measurements were performed at room temperature in the backscattering geometry using 7525 A Kr laser radiation and a Spex third monochromator system. Polycrystalline t-Se and m-Se samples and a small unoriented single crystal of m-Se (α form) were employed. No polarization analysis of the scattered light was performed as similar spectra were observed from both single crystal and polycrystalline m-Se.

III. Results and Discussion

In Fig. (1) the room temperature second order Raman spectrum for m-Se is shown. The dashed lines indicate the wings of the first order peaks which are $\sim 50 - 100$ times more intense. The vertical arrows in Fig. (1) indicate twice the frequency of the k = 0 Raman



Fig. 1. Second order Raman scattering from m-Se(α) at 300 K: The dashed curves indicate wings of the first order spectra while the vertical arrows correspond to twice the frequency of first order k = 0 Raman modes

modes. Above ~35 cm⁻¹ the observed first order spectra are similar to that obtained by Mooradian and Wright (MW) [10], however, additional first order peaks are observed at low frequencies at 16 cm⁻¹, 26 cm⁻¹ and 32 cm⁻¹. The corresponding t-Se second order data for the entire spectral range, which are not shown here, is similar to that reported by MW at low temperature. The latter spectrum was interpreted by Lucovsky et al. [6] in terms of 2k = 0 processes, while Geick and Schröder [11] considered a combined density of states picture. Recent inelastic neutron scattering measurements [7] in t-Se by Gompf indicate, however, that the major second order Raman peaks are to be associated with predominant overtone scattering.

For purposes of discussion the second order spectra of Fig. (1) may be divided into three spectral bands centered at ~180 cm⁻¹, 360 cm⁻¹ and 490 cm⁻¹. The weaker band centered at 360 cm⁻¹ corresponds to combination processes between lower and higher lying optic modes and is similarly observed in t-Se and Te [5]. The other two bands will be assumed in the following discussion to be predominately overtone in character, given the results in t-Se and Te. In contrast to t-Se, the presence of low lying first order optic modes obscures

observation of second order acoustic scattering features in m-Se.

Figure (2) focuses on a comparison of the highest frequency second order band in m-Se with that of t-Se. Note that the onset of



Fig. 2. Comparison of the high frequency second order Raman spectra of m-Se and t-Se at 300 K. The dashed curves indicate the estimated background. Note that the frequency scale is shifted by 20 cm⁻¹ between the two spectra the horizontal axes in Fig. (2) have been shifted by 20 cm^{-1} , while the dashed curves are an estimate of a monotonic background. The spectra clearly indicate substantial changes in the second order scattering that imply appreciable changes in the phonon density of states under the assumption of predominant overtone scattering. While the t-Se spectrum indicates two peaks separated by 20 $\rm cm^{-1}$, the m-Se spectrum also exhibits additional features at 460 cm⁻¹ and 520 cm⁻¹, which occur above and below the major peaks. In m-Se the two major peaks are shifted to higher frequencies relative to t-Se by ~34 cm⁻¹. This corresponds to a first order density of states shift of 17 $\rm cm^{-1}$. This decrease in the average frequency of the highest phonon band in t-Se is attributed to the influence of interchain The absence of interactions. a corresponding strong interaction between rings in m-Se implies that the bond charge and corresponding first neighbor interaction has increased. This is quite analogous to the suggestion in a-Se and a-Te that the absence or reduction of interchain coupling results in a shift of the high frequency band to increasing energies [1,2]. A comparison of the first and second order Raman spectra [12] of bulk a-Se with the results in m-Se indicates a similar shift of the density of states relative to t-Se.

The presence of two similar major peaks in the second order Raman spectra of both m-Se and t-Se implies that their origin is not related to the two peak density of states of a model chain [13], but is a consequency of two-fold coordination. In contrast to m-Se, the t-Se spectra do not indicate additional structure in the phonon spectra at higher frequency. This is attributed to the influence of interchain coupling in the latter which results in a general depression of high frequency phonon states. A similar trend is suggested for Te, where interchain effects are further enhanced [5].

P. J. CARROLL and J. S. LANNIN

At low frequencies the m-Se spectrum of Fig. (1) indicates major peaks at ~162 $\rm cm^{-1}$ and 220 $\rm cm^{-1}$ as well as weak structure between $180 - 220 \text{ cm}^{-1}$. The major peak in m-Se at 220 cm⁻¹ occurs near to twice the frequency of a weak feature observed in the Raman spectra of bulk a-Se [8,10,14] and liquid Se [8]. This feature, which has been attributed to rings [6,8,14] is thus consistent with the density of states peak in m-Se. An earlier analysis [6,14] assumed a totally molecular dispersion for these modes in comparing the k = 0spectra of m-Se and the density of states Raman peak in a-Se. The present results more accurately confirm the consistency of this ring assignment.

A comparison of the second order Raman spectra [12] of a-Se with the results of Fig. (2) indicates much better agreement with the t-Se spectra than that of m-Se. In particular, a broadening of the t-Se spectrum and a shift to higher frequencies as expected for weaker interchain coupling yields an excellent correspondence to the a-Se results. In contrast, the high frequency peak in m-Se at 520 $\rm cm^{-1}$ does not have a corresponding feature in a-Se. This is consistent with a recent analysis based on first order Raman scattering measurements that concluded that chain-like configurations are the dominant scattering entity in a-Se [8]. An exception to this behavior is the weak peak at 110 $\rm cm^{-1}$ which the present results imply arises from a small number of rings.

*Supported in part by NSF Grant DMR 79-08390

References

- 1) R.M. Martin, G. Lucovsky and K. Helliwell: Phys. Rev. B13 (1976) 1383.
- M.H. Brodsky, R.J. Gambino, J.E. Smith, Jr. and Y. Yacoby: Phys. Stat. Sol. (B)52 (1972) 609. P.A. Temple and C.E. Hathaway: Phys. Rev. B7 (1973) 3685. J.S. Lannin, J.M. Calleja and M. Cardona: Phys. Rev. B12 2)
- 3)
- $\tilde{4}$) (1975) 585.
- (1975) 565.
 P.J. Carroll and J.S. Lannin; Proc. 7th International Conference on Raman Spectroscopy, Ottawa, 1980.
 G. Lucovsky, A. Mooradian, W. Taylor, G.B. Wright and R.C. Keezer: Solid State Commun. 5 (1967) 113.
 F. Gompf, in <u>The Physics of Selenium and Tellurium</u>, ed, E. Gerlach and P. Grosse (Springer-Verlag, Berlin, 1979) p. 64.
 P.J. Carroll and J.S. Lannin: J. Non-Cryst. Solids 35-36 (1980) 5)
- 6)
- 7)
- 8) 1277.
- 9) G. Lucovsky and F. Galeener; ibid p. 1209.
- A. Mooradian and G.B. Wright, in <u>The Physics of Selenium and</u> <u>Tellurium</u>, ed. W. C. Cooper (Pergamon Press, New York, 1969) 10)p. 269.
- 11)
- R. Geick and U. Schröder: reference 10, p. 277. J.S. Lannin and P.J. Carroll. Bull. APS 25 (1980) 167, (to be 12) published).
- 13)W. Dultz, H.D. Hochheimer and W. Müller-Lierheim: in Proc. 5th Intern. Conf. Amorphous and Liquid Semicond., ed., J. Stuke and W. Brenig (Taylor and Francis, London, 1974) p. 1281.
 14) M. Gorman and S.A. Solin: Solid State Commun. 18 (1976) 1401.