New vibrational modes in the far-infrared spectra of germanium diselenide

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The polarized transmission and reflectivity spectra of β-$GeSe_2$ are reported in the 20–150 cm^{-1} region. Fourteen A_u and twelve B_u modes have been identified. The results presented improve on those reported earlier. Additional modes have been identified as well.

We reported on the observed Raman and infrared spectra of β-germanium dichalcogenides (GeS_2, $GeSe_2$) in an earlier paper.[1] A crystal and one constituent layer were factor-group analyzed in order to gain insight into the vibrational behavior of these crystals. The existence of Raman-infrared doublets and "rigid-layer" modes yielded an interlayer-to-intralayer bond strength ratio of 100, characteristic of predominantly layered crystals.

The results presented in this Brief Report complement and amend the results published in Ref. 1 as follows.

(a) In Ref. 1, the $P2_1/c$ space group was factor-group analyzed (FGA) on the basis of standard C_{2h} point-group character tables that contain basic functions for $\mathbf{C}_2^y \parallel \mathbf{c}$ usually found in the literature.[2] This not being the case for germanium dichalcogenide, we have corrected the FGA results and defined new experimental conditions for the observation of the infrared and Raman-active modes.

(b) A number of infrared-active modes[1] of germanium diselenide below 150 cm^{-1} were not accurately identified. This was partly due to the resolution of the system (2.5 cm^{-1}), which was insufficient for observations in this region. Thus, we shall now deal predominantly with the above-noted region of the reflectivity and transmission spectra obtained in measurements conducted with much greater resolution, yielding more precise results for the existing lines, and leading to the observation of new infrared-active modes.

Crystal growth, sample preparation, x-ray structure analysis, and sample orientation have been discussed in Ref. 1. A SPECAC far-infrared spectrometer with phase modulation[3] and wire-grid polarizers was used at room temperature to observe transmission and reflectivity spectra from 20–150 cm^{-1}. The spectra were measured with a resolution of 0.325 cm^{-1}.

The β-$GeSe_2$ reflectivity (solid curve) and transmission (dashed curve) spectra in the 20–150 cm^{-1} region are given in Fig. 1. The transmission spectra are given only for $\mathbf{E} \parallel \mathbf{a}$ and $\mathbf{E} \parallel \mathbf{b}$ polarization due to the layer character of the crystals that precluded the cleaving of samples for the measurement of transmission spectra for $\mathbf{E} \parallel \mathbf{c}$.

As can be seen in Fig. 1(a), 10 reflectivity modes were observed. An additional mode was observed in the $\mathbf{E} \parallel \mathbf{a}$ transmission spectra. Eleven modes were observed in the reflectivity spectra for $\mathbf{E} \parallel \mathbf{b}$ with three additional modes be-

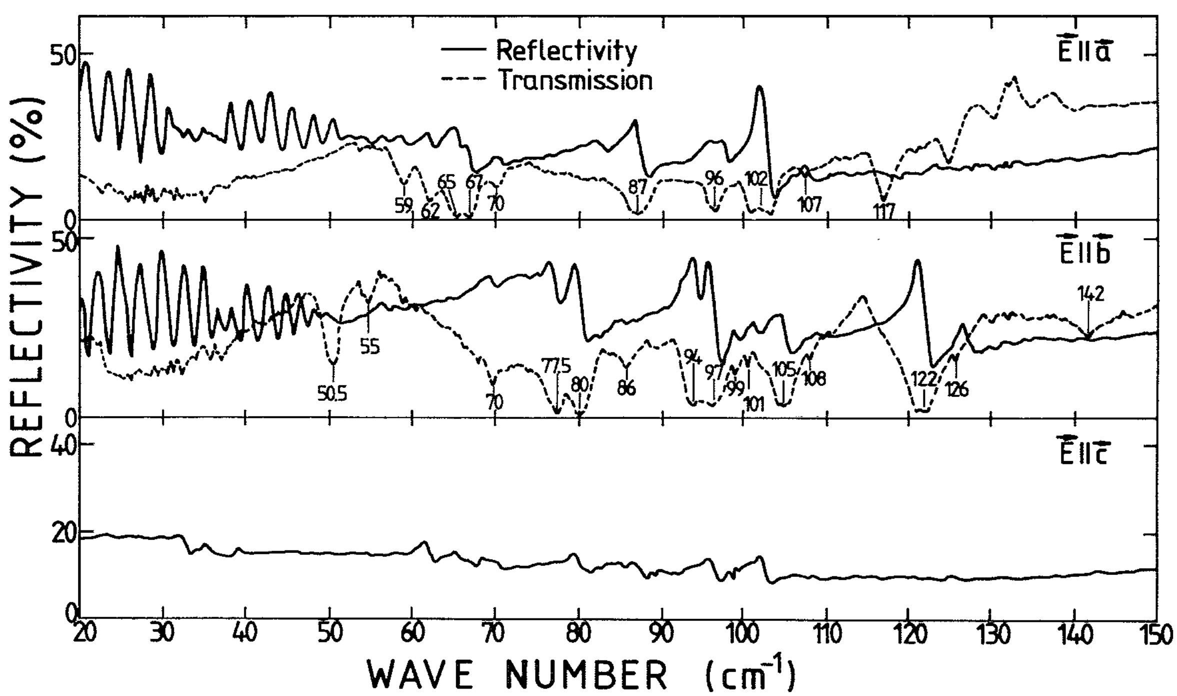

FIG. 1. Reflectivity (solid line) and transmission (dashed line) spectra of β-$GeSe_2$ in the 20–150 cm^{-1} spectral region for $\mathbf{E} \parallel \mathbf{a}$, $\mathbf{E} \parallel \mathbf{b}$, and $\mathbf{E} \parallel \mathbf{c}$ polarization at room temperature.

TABLE I. ir-active mode frequencies (cm^{-1}) of β-$GeSe_2$ in the reflectivity (R) and transmission (T) spectra in Fig. 1 (the upper part of the Table) and from Ref. 1 (lower part of the Table).

A_u E∥b		B_u E∥a		E∥c	
R	T	R	T	R	T
				32	
				35	
				39	
	50.5				
	55				
		59	59		
		62	62	62	
		65	65	65	
					65
		66	67		
70	70	70	70	70	
					71
77	77.5				
80	80			80	
					81
	86	87	87	87	
					88
94	94	93	92		
96	97	96	96	97	
					97
99	99				
101.5	101	102	102	103	
					104
105	105				
	108	108	107		
			117		
					118
122	122				
127	126				
			124		126
	142				166
	197		197		197
	216		216		213
259		262		264	260
276	275	269		278	
		283	282	282	
295	295	298	297	294	
304	305	306	306	304	
			313		
	331			334	342

ing observed in the transmission spectra. A total of 10 modes may be observed for E∥c in Fig. 1(c). The frequencies of these modes, as well as the frequencies of the modes observed above 150 cm^{-1} discussed in Ref. 1, are tabulated in Table I. In conclusion, 20 modes have been observed for E∥a, 22 modes have been observed for E∥b, and 21 modes for E∥c.

Factor-group analysis[1] yields a normal mode distribution at the center of the Brillouin zone of

$$\Gamma = 36A_g(xx,yy,zz,xz) + 36B_g(xy,yz) + 36A_u(\mathbf{E}\parallel\mathbf{b}) + 36B_u(\mathbf{E}\parallel\mathbf{a},\mathbf{E}\parallel\mathbf{c}) \ , \quad (1)$$

where $1A_u + 2B_u$ are acoustic modes, giving $35A_u + 34B_u$ infrared-active modes. As $C_2^y \parallel \mathbf{b}$, the A_u modes may be observed for E∥b, while the B_u modes are observed for E∥a and E∥c.

The observed spectra in Fig. 1 and results of Ref. 1 both yield a total of 22 A_u observed modes, that is, 13 modes fewer than predicted by FGA. The predicted unobserved modes may be too weak to be observed with a 0.325 cm^{-1} resolution. We are of the opinion that a number of the unobserved modes lie in the vicinity of the very strong mode at 259 cm^{-1}, as this was the case for isostructural GeS_2 from 350 to 450 cm^{-1} (Ref. 1). In the case of E∥b, it is not plausible to assume that any modes lie below 50 cm^{-1}, due to the uniformity of the interference fringes. (The thickness of the samples used in the reflectivity measurements was 0.64 mm.) Even a very weak mode would deform and displace the interference pattern.

A comparison of Figs. 1(a) and 1(c) results in the identification of $26B_u$ modes, that is eight modes fewer than predicted by FGA. The unobserved modes are very probably too weak to be observed on our samples and at the resolution of our system.

It is interesting to note that from 30 to 40 cm^{-1} for E∥a, the reflectivity interference patterns become irregular. However, no transmission modes are observed in the above region. Interference fringe irregularities cannot be explained by sample thickness nonuniformity, as the same samples were used for E∥b, for which the fringes were regular.

We are of the opinion that modes exist in the 30–40 cm^{-1} region for E∥a. This is substantiated by modes at 32, 35, and 39 cm^{-1} for E∥c. These modes are the B_u modes predicted by FGA for both E∥c and E∥a. However, as they are very weak, and dipole orientation is such that vibrational modes are best observed for E∥c. For E∥a, their presence merely disrupts the interference fringes in this spectral region. Modes have been observed at almost the same frequencies in Raman spectra of β-$GeSe_2$.[1]

A more detailed analysis of the vibrational behavior of germanium diselenide, based on crystal and layer symmetry considerations and the analysis of molecular vibrational properties of germanium dichalcogenides, has been presented in earlier papers.[1,4–7]

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