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### LATTICE MODES IN THE LINEAR CHAIN COMPOUND ZrTe,

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We report Raman scattering experiments on the linear chain compound  $ZrTe_5$ . Room and low temperature measurements rule out the existence of a structural phase transition, suggested by the resisitive anomaly near 150 K. The eight  $\vec{k} = \vec{0}$  vibrationnal modes allowed by the scattering geometry are observed and their symmetries determined from polarized spectra. Some of the modes are identified on the basis of symmetry properties and (or) in comparison with the Raman spectra of the related compound  $ZrTe_3$ . Moreover, this comparison indicates surprisingly similar strengths for atomic interactions in  $ZrTe_3$  and  $ZrTe_5$ .

#### Introduction

ZrTe<sub>5</sub> crystallizes in a chain structure <sup>1</sup> closely related to that of the transition-metal trichalcogenides. In some of these low dimensional compounds, such as NbSe<sub>3</sub>, a particular form of the Fermi surface produces electronic instabilities which drive structural phase transitions <sup>2</sup>,<sup>3</sup>. This explains the recent attention devoted to the pentatellurides ZrTe<sub>5</sub> and HfTe<sub>5</sub> <sup>4</sup> and the subsequent investigation of their structural and transport properties by means of various techniques. In spite of a resistive anomaly <sup>5</sup> observed near 150 K, the other measurements <sup>4</sup> ruled out the possibility of an electronically-driven phase transition similar to that reported in NbSe<sub>3</sub>.

In the present paper, we report the results of room and low temperature Raman scattering experiments on crystalline ZrTe<sub>5</sub>. The crystal structure is described in Sec. 2. The experimental details are given in Sec. 3. Following the factor group analysis of the crystal and chain  $\vec{k} = \vec{0}$  vibrationnal modes, the experimentally observed spectra are presented and discussed in Sec. 4.

#### 2. Crystal Structure

ZrTe<sub>5</sub> was shown to be isostructural with HfTe<sub>5</sub>, the crystal structure of which has been determined by the X-ray work of Furuseth et al.<sup>1</sup> ZrTe<sub>5</sub> crystallizes in the Cmcm ( $D_{17}^{17}$ ) space group. The conventional non-primitive unit cell contains four formula units and has the dimensions a = 3.9876 Å, b = 14.502 Å and c = 13.727 Å.

 $ZrTe_5$  possesses an interesting structure with both layer and chain features that are responsible for the easy (010) cleavage and the fibrous looking of the crystals. Fig. 1(a) shows projections of the structure into different crystallographic planes, and displays the 12-atom primitive unit cell, with two chains passing througn. One can build up the infinite atomic chains parallel to the a axis by stacking together distorted bicapped trigonal prisms of tellurium with the zirconium atoms located in the centre. The chains are linked by Te-Te bonds so as to form layers approximately parallel to the (010) plane. The layers are held together by weak Van der Waals-type forces.

This structure is closely related to that of  $ZrTe_3$  <sup>6</sup> and other  $IV_b$  transition-metal trichalcogenides. The main difference, which accounts for the difference in composition, lies in the linkage between the basic coordination units [see fig. 1(b)].

#### 3. Experiment

The samples studied in this work were single crystals of  $ZrTe_5$ , with typical dimensions  $6 \times 0.2 \times 0.4 \text{ mm}^3$ . The Raman measurements were taken on freshly cleaved (010) surfaces in order to avoid scattering from Te, left behind by surface oxidation. The prepared samples were immediately immersed in the exchange gaz of an Oxford CF 204 cryostat for room and low temperature experiments.

The Raman spectra of ZrTe<sub>5</sub>, excited with the 5145 Å and 5309 Å lines of *Spectra Physics* argon and krypton ion lasers, were measured in the backscattering geometry. The laser beam was focused onto the surface sample at nearly normal incidence. The scattered light was collected along the crystal b axis direction and analyzed in a *T800 Coderg* triple monochromator, in conjunction with standard photoncounting electronics.





- Fig.1. Structure of ZrTe, type crystals (a) Projections in the (001) and (100) planes. The primitive unit cell is shown on the top
  - diagram. The crystal-symmetry elements are indicated on both diagrams.
- (b) Interchain linkage in ZrTe5, compared to that in ZrTe3. The principal axes X, Y, Z are chosen to coïncide with the crystallographic axes

4. Results and Discussion

a, b, c.

### 4.1. Factor group analysis

The crystal factor-group contains the eight representative symmetry elements :

1 : the identy,

- $2_{a}$ ,  $2_{b}$  : twofold axes parallel respectively to the a and b axes,
  - $2_c$ : a twofold screw axis parallel to c,  $\overline{1}$ : a centre of symmetry,

 $\bar{z}_{e}$ ,  $\bar{z}_{c}$ : mirror planes perpendicular respectively to a and c,

 $\bar{2}_{b}$  : a glide plane perpendicular to b.

Four of these symmetry elements (the identi-ty, the  $2_b$  twofold axis and the  $\overline{2}_a$ ,  $\overline{2}_b$  mirror planes) are in common with the factor group of a single chain.

The symmetries of the long-wavelength phonons are determined by the representation  $\Gamma_{\rm crystal}$  of the crystal factor group generated by the displacements of the atoms in the primitive unit cell.

r<sub>crystal</sub> is 36 dimensional for the 12-atom primitive unit cell of ZrTe5. The reduction of crystal into irreducible representations of the isomorphic point group mmm  $(D_{2h})$  is as follows :

$$\Gamma_{\text{crystal}} = \frac{6A_g}{4} + \frac{6B_{3g}}{4} + \frac{2B_{2g}}{4} + \frac{4B_{1g}}{4} + \frac{6B_{2u}}{4} + \frac{4B_{3u}}{4} + \frac{6B_{1u}}{4}$$

Because of the inversion operation contained in the crystal factor-group, Raman and infra-red activities are mutually exclusive. The eighteen even-parity modes are optical Raman active phonons, while the eighteen odd-parity modes consist of three acoustical and fifteen optical infra-red active phonons. The k = 0 modes can further be classified according to atomic displacements, parallel to the chains (or out-of- $\overline{2}_a$  mirror plane) for  $B_{1g}$ ,  $B_{2g}$ ,  $B_{3u}$ ,  $A_u$  symmetries and perpendicular to the chains (or in  $-\overline{2}_a$  mirror plane) for Ag, B3g, B2u, B1u.

Since the chains constitute well-defined

units in the crystal, it is convenient to first look at the long-wavelength modes of a single chain and then establish a compatibility relationship connecting the chain to the crystal. The chain factor-group representation  $\Gamma_{\rm chain}$ generated by the displacements of atoms in the 6-atom primitive unit cell is 18 dimensional, and reducible into irreducible representations of the isomorphic point group 2mm (C<sub>2V</sub>):

 $\Gamma_{chain} : 6A_1 + 6B_1 + 2A_2 + 4B_2$ 

Due to the lack of a centre of symmetry, the long-wavelength optical modes of the chain are not divided into even -and odd- symmetry types. The chains modes can be classified according to atomic displacements in -or out- of  $\overline{2}_{a}$ mirror plane, corresponding respectively to indices 1 and 2. A and B stands for modes respectively symmetric and antisymmetric with respect to the twofold rotation. The correlation method was used to relate the irreducible representations of the zirconium and tellurium atoms site groups to those of the chain factor group. From the correlation chart presented in table I(a), we can determine which atoms move in each normal mode and wether this motion is along or perpendicular to the chain axis.

Table I(b) displays the correlation diagram relating the long-wavelength chain and crystal phonons in ZrTe<sub>5</sub>. Since there are two chains per primitive unit cell correlated via an inversion centre, each chain mode splits into a g-u pair in the crystal. Furthermore, because the crystal retains all the symmetry elements of the chain, there is no mixing of the chain modes symmetries in the crystal.

In particular, the A and B symmetries do not mix, in contrast to what happens in the monoclinic structure of the IV<sub>b</sub> metal-transition trichalcogenides. Lastly, as a result of the interchain coupling, the  $A_1 + 2B_1 + B_2$  zero frequency modes of the chain divide up into four odd crystal modes (three acoustical  $B_{2u} + B_{1u} + B_{3u}$  and one infra-red  $B_{1u}$ ) and four low-lying even modes  $A_g + 2B_{3g} + B_{1g}$ . These Raman active modes are expected to be largely rigid chain motions. They can be classified in three translational modes  $B_{1g}$ ,  $A_g$ ,  $B_{3g}$  respectively along the a-, b- and c axes, and a librationnal mode  $B_{3g}$ 

4.2. Experimental results and discussion

In the XYZ set of principal axes, chosen sc as to coincide with the abc crystallographic axes of the crystal, the polarizability tensors <sup>7</sup> of the  $\vec{k} = \vec{0}$  Raman-active modes of ZrTe<sub>5</sub> have the form :

	a		.a.	e	[]
Ag:	.ъ.	B <sub>1</sub> ;	d	$B_{2\sigma}$ :	B <sub>30</sub> :f
	c	.6		-° le	<sup>76</sup> .f.

The backscattering geometry described in 3 allows the measurements of Raman tensor components XX, ZZ, XZ. Thus six  $A_g$  and two  $B_{2g}$  modes should be experimentally observed among the eighteen modes theoretically predicted.

Fig. 2 shows unanalyzed Raman spectra for two temperatures, above and below 150 K. As can be seen, eight peaks are clearly observed at room temperature. No new peak occurs at low temperature that would reveal any change of the crystallographic unit cell, such as those induced by charge density waves in many layered transition dichalcogenides <sup>8,9</sup>.

The different components of Raman tensor allowed by the scattering geometry are shown in Fig. 3, which depicts modes polarized respectively parallel  $(B_{2g})$  and perpendicular  $(A_g)$  to the chains. The symmetries and wavenumbers of the observed  $\vec{k} = 0$  Raman active modes are given in Table II.

We shall approach the mode assignment from the analysis of the single chain vibrations, substantiated by a comparison with the Raman spectra of  $2rTe_3$ . We present in Table III the list of k = 0 phonons in  $2rTe_3$  and their assignment to chain modes according to the Raman works of Zwick et al.<sup>10</sup>, and Wieting et al.<sup>11</sup>.

As it appears from the comparison of Table III, the longwavelength phonons of ZrTe<sub>5</sub> lye very near in frequency to those of ZrTe<sub>3</sub>. Beyond the close relation between the two structures, this provides evidence of similar strengths for atomic interactions in the two compounds.

Considering first in ZrTe5 the two B2 modes polarized along the a axis, we see from Table I(b) that they originate from  $A_2$  chain modes. Table I(a) shows that these A<sub>2</sub> modes are mixtures of shearing motions of the  $Te_{II}$  and  $Te_{III}$  pairs respectively. In the crude model of bond stretching forces between nearest neighbours in the chain, the shearing motion of Te<sub>III</sub> atoms does not imply any stretching of the Zr-Te<sub>III</sub> bonds, which are perpendicular to the chains. The interchain coupling rises this zero frequency mode until it mixes with the shearing mode of the Tell pair, which depends essentially on intrachain Zr-Te<sub>II</sub> interaction. Assuming the same interaction between Zr and TeII atoms within the chains in ZrTe3 and ZrTe5, we expect in ZrTe5 a B2g crystal doublet, very close in frequency

to the B mode of ZrTe<sub>3</sub> originating from the shearing  $\delta f$  the Te<sub>II</sub> pair in the chain. The B<sub>2</sub>g spectrum of ZrTe<sub>5</sub> (Fig.3) exhibits clearly a doublet of lines lying respectively at 74 and 89.5 cm<sup>-1</sup>, close in frequency to the single Bg mode observed at 68 cm<sup>-1</sup> in ZrTe<sub>3</sub>. The Raman study of ZrTe<sub>5</sub> thus substantiates in turn mode assignment in ZrTe<sub>3</sub> : we confidently attribute to A<sub>2</sub> chain mode the 68 cm<sup>-1</sup> line in ZrTe<sub>3</sub>, in agreement with previous assignment by Wieting and coworkers <sup>11</sup> based on the line intensity.

Looking now at the six Ag modes of ZrTe5, we refer back to Table I(b) and conclude that they all proceed from A1 chain modes. According to theoretical expectations, we assign the lowest lying line at 39  $\rm cm^{-1}$  to the quasi-rigid translationnal motion of the chains along the b-axis. Its wavenumber is surprinsingly close to that of the lowest A mode in  $ZrTe_3$  (37 cm<sup>-1</sup>), which was attributed too to a translationnal chain mode of the crystal. This might prove in turn the A<sub>1</sub> symmetry of the 37 cm<sup>-1</sup> line of  $ZrTe_3$ , as we proposed in earlier work <sup>10</sup>. The highest frequency line at 239 cm<sup>-1</sup> is attributed to the stretching mode of the diatomic (Te<sub>II</sub>)2"molecule" This mode lies at slightly higher frequency than the corresponding mode of ZrTe3 (217 cm<sup>-1</sup>), that would indicate stronger atomic interaction and shorter covalent bond length between the pairing  $Te_{II}$  atoms in ZrTe5 than in ZrTe3. As for the others Ag lines, such a qualitative discussion

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Table I.

- (a) Correlation chart between  $C_{2V}$  and  $C_{S}$  site (a) correlation that between Te2V and te3 site groups of (Zr, Te1) and (Te11, Te111) atoms and C<sub>2V</sub> chain factor group in ZrTe5.
  (b) Compatibility diagram relating the chain and crystal vibrations of ZrTe5.





Table II. Wavenumbers and symmetries of  $\vec{k} = \vec{0}$ Raman active phonons of ZrTe<sub>5</sub> at 300 K and 77 K.

Chain	A <sub>1</sub>	<sup>A</sup> 2	A2	A 1	A <sub>1</sub>	A 1	<sup>А</sup> 1	A 1
Crystal	Ag	B <sub>2g</sub>	<sup>B</sup> 2g	Ag	Ag	Ag	Ag	Ag
300 K	39	72	86.5	116	121	147	181.5	
77 K	40	74	89.5	117	123	152	183.5	239
	Chain Crystal 300 K 77 K	Chain         A1           Crystal         Ag           300 K         39           77 K         40	Chain         A1         A2           Crystal         Ag         B2g           300 K         39         72           77 K         40         74	Chain         A1         A2         A2           Crystal         Ag         B2g         B2g           300 K         39         72         86.5           77 K         40         74         89.5	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



Fig.2. Unpolarized Raman spectra of  $\text{ZrTe}_5$  excited with  $\lambda = 5145$  Å at 300 K and 77 K. The structures marked by an asterisk are due to scattering by A<sub>1</sub> and E modes of crystalline Te, left behind by surface oxidation.

Ref	. 11		Ref. 10				
Sym	metry		Symme				
Crystal	Chain	(em ) _	Crystal	Chain	v (em )		
Ag	$B_1(T_X)$	11					
Ag	$B_1(R_y)$	38	Ag	$A_1(T_Z)$	37.5		
A,	$A_1(T_Z)$	62	Ag	$B_1(T_x)$	61.5		
Bg	A <sub>2</sub>	64	Bg		66.5		
Ag	B <sub>1</sub>	86	Ag	$B_1(R_y)$	84.5		
A _	A <sub>1</sub>	108	Ag	A <sub>1</sub>	111		
Å,	A <sub>1</sub>	144	Ag	A,	143.5		
Ag	А <sub>1</sub>	216	Ag	A <sub>1</sub>	215		

Table III. Wavenumbers and symmetries of  $\vec{k} = \vec{0}$ Raman active phonons of ZrTe<sub>3</sub> at 300 K.



Fig.3. Polarized Raman spectra of ZrTe<sub>5</sub> excited with  $\lambda$  = 5309 Å at 77 K.

is not sufficient, and an interatomic-force model is needed to describe the lattice dynamics of ZrTe<sub>5</sub> and calculate the eigenvectors of the corresponding modes.

#### 3. Conclusion

The Raman study of crystalline  $\text{ZrTe}_5$  at room and liquid nitrogen temperatures rules out the possibility of an electronically driven phase transition near 150 K suggested by a resistive anomaly. All the k = 0 phonons predicted by group theory analysis and allowed by the scattering geometry have been observed, and their symmetry determined by polarization measurements. An approach of the crystal lattice dynamics from the "molecular" point of view allows the identification of some crystal modes, in absence of complete calculation based on an interatomic-force model. The comparison with the Raman spectra of the closely related compound ZTTe<sub>3</sub> demonstrates that, in spite of the dissimilarity in internal architecture of the basic layers, the strengths of atomic interactions are similar in the two compounds.

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