Structural contributions to the pressure-tuned charge-density-wave to superconductor transition in ZrTe$_3$: Raman scattering studies


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Structural contributions to the pressure-tuned charge-density-wave to superconductor transition in ZrTe₃: Raman scattering studies

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Superconductivity evolves as functions of pressure or doping from charge-ordered phases in a variety of strongly correlated systems, suggesting that there may be universal characteristics associated with the competition between superconductivity and charge order in these materials. We present an inelastic light (Raman) scattering study of the structural changes that precede the pressure-tuned charge-density-wave (CDW) to superconductor transition in one such system, ZrTe₃. In certain phonon bands, we observe dramatic linewidth reductions that accompany CDW formation, indicating that these phonons couple strongly to the electronic degrees of freedom associated with the CDW. The same phonon bands, which represent internal vibrations of ZrTe₃ prismatic rods, are suppressed at pressures above ~10 kbar, indicating a loss of long-range order within the rods, specifically amongst intrarod Zr-Te bonds. These results suggest that the pressure-induced suppression of CDW order observed in ZrTe₃ is structurally driven, and provide insights into the origin of pressure-induced superconductivity in this material.

One of the most exciting areas of condensed matter research involves the study of how superconductivity evolves from magnetic- or charge-ordered phases in a diverse range of strongly correlated systems, including high Tc cuprates,¹ iron-arsenide superconductors,² and charge density wave materials.³–⁶ While the presence of secondary ordered phases are generally inimical to superconductivity in conventional superconductors, there is growing evidence that the optimal conditions for superconductivity in some unconventional superconductors may require some phase competition, and perhaps even phase coexistence.¹,⁶

A particularly interesting group of materials in which phase competition between charge and superconducting order appears to be important is charge-density-wave (CDW) materials that can be tuned to superconductor phases with either pressure or intercalation. Examples of these systems include intercalated¹ and pressure-tuned³ 1T-TiSe₂, intercalated TaS₂,⁷ pressure-tuned TbTe₃,⁸ intercalated HoTe₃,⁹ and intercalated¹⁰,¹¹ and pressure-tuned¹² ZrTe₃. These systems offer the opportunity to explore the competition between charge-order and superconductivity,³–⁶ and particularly the structural changes that enable the emergence of superconductivity as the CDW state collapses with increasing pressure or intercalation.

ZrTe₃ crystallizes in the ZrSe₃-type structure (space group P2₁/m, shown in Fig. 1) in which ZrTe₃ trigonal prisms stack along the b axis to form infinite quasi-one-dimensional rods.¹³ The monoclinic unit cell contains two such rods, which are related by screw symmetry. Interprism Zr-Te bonds hold the rods together to form layers in the ab-plane which are easily cleaved along the c axis. Within each layer, Te(2) and Te(3) atoms form a dimerized chain along the a axis.¹³

Electronically, ZrTe₃ exhibits an anisotropic metallic resistivity below 300 K (ρ₀ ∼ ρₐ ∼ ρ₈/10),¹¹,¹⁴ and has resistive anomalies associated with CDW formation at TCDW = 63 K¹⁴ and filamentary superconductivity below Tc = 2 K.¹⁵ The CDW transition in ZrTe₃ is associated with a commensurate structural modulation of wavevector q = (1/14,0,1/3),¹¹,¹⁴,¹⁶ and most

FIG. 1. (Color online) ZrTe₃ crystal structure. (left) Projection onto the ab plane. The dotted line represents the cleavage plane in this material. (right) Perspective showing two ZrTe₃ prismatic rods.
strongly affects the conductivity perpendicular to the prismatic rods. A Kohn anomaly associated with a soft phonon mode—-as well as CDW fluctuations that extend well above \( T_{CDW} \)--have been identified with the CDW transition in ZrTe$_3$. Both band structure calculations and angle-resolved photoemission spectroscopy measurements indicate that the dimerized chains of Te(2)-Te(3) atoms along the a axis yield quasi-1D electronlike sheets of Fermi surface, and that nesting of these sheets may be responsible for CDW formation.

The application of hydrostatic pressure initially increases \( T_{CDW} \) with increasing pressure up to \( \sim 10 \) kbar (1 GPa), but increasing the pressure above \( \sim 20 \) kbar suppresses \( T_{CDW} \), eventually leading to a complete suppression of CDW order above 50 kbar. Increasing hydrostatic pressure also initially suppresses superconductivity for pressures greater than 5 kbar, but reentrant superconductivity is observed for pressures above 50 kbar, i.e., above the pressure at which CDW behavior is suppressed. Cu- and Ni-intercalation have also been shown to suppress the charge density wave state and induce superconductivity in ZrTe$_3$.

While much is known about the complex phase diagrams of pressure-tuned and intercalated ZrTe$_3$ systems, several key issues concerning the underlying mechanisms governing the CDW-to-superconductor transitions remain uncertain. In particular, neither the relationship between the collapse of CDW order and the emergence of superconductivity in these systems, nor the nature of the structural changes that accompany this evolution, are well understood. These unresolved issues—which also confront a much broader range of materials exhibiting CDW-to-superconductor transitions—provide impetus for investigating the CDW-to-superconductor transition in ZrTe$_3$ using methods capable of probing the underlying structural changes associated with this transition.

We have used variable-temperature and variable-pressure inelastic light (Raman) scattering to investigate the microscopic details underlying the pressure-induced phases of ZrTe$_3$. Phonon Raman scattering is particularly effective for studying the complex structural phases and changes in electron-phonon coupling that accompany temperature- and pressure-dependent phase changes in correlated materials such as ZrTe$_3$, because this technique can convey detailed information about changes associated with specific atomic elements of the unit cells. In this paper, we show that certain phonon bands undergo dramatic linewidth reduction near \( T_{CDW} \), indicating that these phonons couple strongly to the electronic degrees of freedom associated with the CDW. The same phonon bands, which represent internal vibrations of the ZrTe$_3$ prismatic rods, are suppressed at pressures above \( \sim 10 \) kbar. This indicates a pressure-induced loss of long-range order within the rods, specifically amongst intrarod Zr-Te bonds. We also find structural evidence for pressure-induced dimensional crossover in ZrTe$_3$. These results suggest a structural mechanism for the observed suppression of CDW formation above \( \sim 20 \) kbar and provide insights into the origin of pressure-induced superconductivity in ZrTe$_3$.

II. EXPERIMENT

A. Sample preparation

Single crystals of ZrTe$_3$ were prepared at Brookhaven National Laboratory by chemical vapor transport, using a nearly stoichiometric mixture of powdered Zr and Te that was enclosed in an evacuated and sealed quartz ampoule along with iodine as the transport agent. The furnace gradient was kept between 760 and 650 C after heating to 700 C for two days. Crystals were oriented using a Panalytical X'pert single-crystal x-ray diffractometer with Cu K$_{α1}$ radiation.

B. Raman scattering measurements

Raman scattering measurements were performed using the 647.1 nm excitation line of a Kr$^+$ laser. The incident laser power was limited to 5 mW and was focused to a \( \sim 50 \) μm-diameter spot to minimize laser heating of the samples; consequently, it was assumed that there was a negligible increase in the sample temperature from laser heating. The scattered light from the samples was collected in a backscattering geometry, dispersed through a triple-stage spectrometer, and then recorded with a liquid-nitrogen-cooled CCD detector. The incident light polarization was selected with a polarization rotator, and the scattered light polarization was analyzed with a linear polarizer, providing symmetry information about the excitations studied.

Variable-pressure and variable-temperature measurements were performed using a miniature cryogenic diamond anvil cell inserted into a helium-flow-through cryostat. This high pressure cell allows for in situ pressure adjustment, enabling Raman scattering measurements at temperatures 3–300 K and pressures 0–100 kbar. A liquid-argon medium was used to provide quasi-hydrostatic pressure. The pressure was determined from the shift in the R$_1$ fluorescence line of a ruby placed near the sample.

III. RESULTS AND DISCUSSION

A. Identification of phonon modes in ZrTe$_3$

Raman scattering has been used previously to measure the phonon spectrum of ZrTe$_3$ at room temperature and at \( T = 77 \) K. Fig. 2 shows our measurements of the phonon spectra of ZrTe$_3$ at \( T = 295 \) K and \( 6 \) K, obtained in a \( (\mathbf{E}_i, \mathbf{E}_o) = (a, a) \) scattering geometry, where
Ei and Es are the incident and scattered light polarization directions, respectively. The T = 295 K phonon spectrum of ZrTe3 exhibits six first-order phonon modes at ω1 = 38 cm\(^{-1}\), ω2 = 60 cm\(^{-1}\), ω3 = 84 cm\(^{-1}\), ω4 = 108 cm\(^{-1}\), ω5 = 144 cm\(^{-1}\) and ω6 = 215 cm\(^{-1}\). These energies are similar to those obtained previously.\(^{24,25}\)

As mentioned, the ZrTe3 crystal may be viewed as infinite rods of ZrTe3 trigonal prisms that are held together by interprism Zr-Te bonds. The phonon spectra of isostructural crystals ZrS3 and ZrSe3 are comprised of two sets of three vibrations that are well separated in energy,\(^{25}\) encouraging a normal mode description that discriminates between ‘external’ or prismatic-rod-preserving vibrations, and ‘internal’ or prismatic-rod-distorting vibrations. Although the two sets of vibrations are not as well separated in ZrTe3 (see Fig. 2), we nevertheless follow previous authors\(^{23,24,26}\) in assigning lower-energy modes ω1-ω3 to primarily external vibrations of the trigonal prismatic rods, and higher-energy modes ω4-ω6 to primarily internal vibrations of the trigonal prismatic rods. These assignments are supported by the distinct pressure dependences of the external and internal mode frequencies (see section III C), as well as the symmetry considerations described below.

In the limit of weak interrod bonding, such that the 2\(\overline{mm}\) symmetry of the rods predominates, the (\(a,a\)) scattering geometry used in this experiment allows for the observation of only 3 \(A_1\) internal vibrations. One of these, a ‘diatomic’ vibration of the Te(2)-Te(3) bond, is assigned to ω6 following previous lattice dynamical calculations.\(^{26}\) The other two internal vibrations, which involve deformations of the trigonal prisms along the c axis, are assigned to ω4 and ω5. As interrod bonding becomes more significant, the 2\(/m\) crystal symmetry allows for the observation of up to five additional vibrations (\(A_1 + 4 B_2\)) in the (\(a,a\)) scattering geometry, including three external vibrations of the prismatic rods.\(^{27}\) These rod preserving modes are assigned to the relatively weaker, lower energy modes ω1-ω3.

In addition to the sharp phonon modes shown in Fig. 2, at T = 295 K there is a broad background that is likely associated with inelastic electronic scattering. This interpretation is supported by the broad linewidths of the ω4 and ω5 phonon modes, and especially by the asymmetric Fano lineshape of the ω4 phonon mode, suggesting that these modes are particularly strongly coupled to the underlying electronic background.

Several weak features appear in the T = 6 K spectrum, for example the peaks between ω = 175-200 cm\(^{-1}\). These features likely represent phonons that have been folded to k = 0 from elsewhere in reciprocal space due to the CDW modulation of the structure. As can be seen in the following sections, these peaks vanish when the system is tuned out of the CDW phase via either temperature or pressure.

B. Temperature dependence of phonon modes in ZrTe3

The temperature dependence of the Raman spectrum of ZrTe3 is shown in Fig. 3(a), with the temperature dependence of the phonon band linewidths summarized in Fig. 3(b). The rigid rod phonon modes ω2 and ω3, along with the diatomic mode ω6, show little linewidth dependence on decreasing temperature. On the other hand, vibrations ω4 and ω5, which involve deformations of the ZrTe3 trigonal prisms along the c axis, exhibit dramatic changes in linewidth as a function of decreasing temperature. In particular, between T = 200 K and 5 K the linewidths of the ω4 and ω5 bands decrease by factors of \(\sim 4.5\) and \(\sim 3.5\), respectively (see Fig. 3(b)). The spectral range considered in this experiment did not include the lowest-energy external mode ω1.

The large reduction in linewidth of the ω4 and ω5 bands that accompanies CDW formation indicates a strong coupling between these vibrations and the electronic states associated with the CDW. As mentioned, CDW modulation in ZrTe3 opens a gap 2\(\Delta\) in the dispersion of the electronic band arising from the 5p orbitals of Te(2) and Te(3) ions.\(^{13,29}\) The size of 2\(\Delta\) was found to be at least 400 cm\(^{-1}\), i.e., larger in energy than the vibrations considered here. Therefore, the reduction in linewidth of modes ω4 and ω5 as the gap is opened reflects a loss of electronic relaxational channels for these particular vibrations. Such linewidth changes have also been ob-
served for strongly coupled phonons in other correlation gap materials, such as the putative Kondo insulator FeSi and the A-15 superconductor Nb$_3$Sn. On the other hand, the lower-energy external vibrations are evidently not strongly coupled to the relevant electronic degrees of freedom, as their linewidths are insensitive to the formation of the CDW (see Fig. 3(b)). Remarkably, the linewidth of the diatomic vibration $\omega_6$ is also largely insensitive to the electronic gap formation, despite the fact that this mode represents a longitudinal vibration of the dimerized Te(2)-Te(3) chain.

### C. Pressure dependence of phonon modes in ZrTe$_3$

The pressure dependence of the Raman spectrum of ZrTe$_3$ is shown for $T = 3$ K in Fig. 4(a), with the pressure dependences of the $\omega_2 - \omega_6$ mode frequencies summarized in Fig. 4(b). The frequencies of internal modes $\omega_1 - \omega_6$ show relatively little sensitivity to applied pressure, while the frequencies of external modes $\omega_2$ and $\omega_3$, which stretch the interrod Zr-Te bonds, increase linearly as a function of pressure. This indicates that interrod coupling becomes stronger at high pressures, or equivalently, that the crystal becomes more three-dimensional. Increased three-dimensionality and the resultant reduction in nested Fermi surface has been speculated to contribute to the pressure-induced suppression of the CDW above $\sim 20$ kbar in ZrTe$_3$. Similar pressure-induced transitions between CDW and superconducting phases caused by enhanced interrod coupling have also been observed in the quasi-1D rod materials NbSe$_3$ and Nb$_3$Te$_4$. The decreased one-dimensionality of ZrTe$_3$ with pressure also suggests that pressure-induced superconductivity in ZrTe$_3$ will not have the filamentary nature that characterizes the ambient pressure superconductivity.

The most striking feature of the spectra shown in Fig. 4(a) is the suppression of internal vibration peaks $\omega_4$ and $\omega_5$ with applied pressure. Whereas warming through the CDW transition broadens peaks $\omega_4$ and $\omega_5$ by a factor of $3.5 - 4.5$ due to an increase in carriers, increasing pressure has a much smaller ($<50\%$) effect on the linewidths of these peaks. The pressure-induced loss of integrated intensity of peaks $\omega_4$ and $\omega_5$ is therefore most likely due to a loss of long-range structural order, rather than over-damping due to electron-phonon coupling. To be more specific, we note that the suppressed modes $\omega_4$ and $\omega_5$ primarily stretch intraprism Zr-Te bonds. On the other
hand, the lower-energy external vibrations \( \omega_2 \) and \( \omega_3 \), which primarily involve interprism Zr-Te bonds, as well as the diatomic vibration \( \omega_5 \) of the Te(2)-Te(3) bond, all persist up to the highest pressures measured. Therefore, the pressure-induced loss of long-range order and suppression of modes \( \omega_4 \) and \( \omega_5 \) is likely due to disorder amongst the intraprism Zr-Te bonds.

Figure 5(b) shows the pressure-dependence of the peak intensity of the \( \omega_5 \) band, relative to the robust \( \omega_6 \) band. For comparison, Fig. 5(a) shows the evolution of \( T_{CDW} \) (filled circles) as a function of pressure. The peak intensity decreases rapidly above \( \sim 10 \text{ kbar} \), and is almost completely suppressed at pressures approaching the CDW collapse at \( \sim 50 \text{ kbar} \). Since the \( \omega_4 \) and \( \omega_5 \) vibrations have already been shown to be strongly coupled to the electronic degrees of freedom involved in CDW formation, and since the suppression of \( T_{CDW} \) follows the suppression of modes \( \omega_4 \) and \( \omega_5 \), it is natural to associate the disorder amongst intraprism Zr-Te bonds with the collapse of the CDW. In support of this interpretation, we note that a recent ambient-pressure study of single-crystal ZrTe\(_3\) grown at elevated temperatures also observed suppression of the CDW in favor of superconductivity.\(^{35}\) This was attributed to random displacements of the Zr and Te(1) atoms along the \( c \) axis as measured with x-ray diffraction, which is an interpretation quite similar to the pressure-induced structural changes proposed in our study. High-pressure x-ray-diffraction measurements of pure ZrTe\(_3\) would be useful for confirming this interpretation of our high-pressure results.

The pressure dependences of the ZrTe\(_3\) optical phonons demonstrate not only a trend toward higher-dimensionality, which may explain the pressure-induced suppression of the CDW in general terms via a loss of nested Fermi surface, but also indicate a specific structural change that appears to precede CDW collapse; namely, a loss of long-range order in the ZrTe\(_3\) trigonal prismatic rods.

IV. SUMMARY

We have performed variable-temperature Raman measurements of ZrTe\(_3\) which show that certain ZrTe\(_3\)-rod-deforming vibrations exhibit dramatic linewidth reductions that accompany CDW formation in this crystal, indicating that these vibrations are strongly coupled to the electronic states involved in the formation of the CDW. We have also performed variable-pressure Raman measurements which show that the same ZrTe\(_3\)-rod-deforming vibrations are strongly suppressed at pressures above \( \sim 10 \text{ kbar} \), mirroring the previously-observed pressure-induced suppression of the CDW. We argue that this suppression reflects a loss of long-range structural order at high pressures, specifically amongst the intrarod Zr-Te bonds, and that such a structural degradation may be responsible for the eventual pressure-induced collapse of the CDW.

Note added in proof. As this manuscript was in submission, we became aware of a variable-temperature Raman investigation of the ZrTe\(_3\) vibrational modes by Hu et al. which shows good agreement with our variable-temperature experimental results.\(^{36}\) Their calculation of the normal mode displacement patterns indicates that modes \( \omega_4 \) and \( \omega_5 \) have some longitudinal character along the \( a \) axis, i.e., stretch the Te(2)-Te(3) bonds. This may explain the strong coupling between these vibrations and the gapped electronic states, as the polarization of the soft phonon in ZrTe\(_3\) has a large component along this direction.\(^{17}\) It may also mean that the structural degradation that instigates the suppression of CDW order involves the Te(2)-Te(3) bonds in addition to the intrarod Zr-Te bonds. Our essential conclusion—that the pressure-tuned CDW-to-superconductor transition in ZrTe\(_3\) appears to be structurally driven—remains unchanged.
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