Quantum Melting of the Charge-Density-Wave State in 1T-$TiSe_2$

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(Received 8 April 2003; published 24 September 2003)

We report a Raman scattering study of low-temperature, pressure-induced melting of the charge-density-wave (CDW) phase of 1T-$TiSe_2$. Our measurements reveal that the collapse of the CDW state occurs in three stages: (i) For $P < 5$ kbar, the pressure dependence of the CDW amplitude mode energies and intensities are indicative of a "crystalline" CDW regime; (ii) for $5 < P < 25$ kbar, there is a decrease in the CDW amplitude mode energies and intensities with increasing pressure that suggests a regime in which the CDW softens, and exhibits enhanced fluctuations; and (iii) for $P > 25$ kbar, the absence of amplitude modes reveals a metallic regime in which the CDW has melted.

DOI: 10.1103/PhysRevLett.91.136402 PACS numbers: 71.30.+h, 71.45.Lr, 78.30.–j

There has been a great deal of interest in the relationship between various diverse and exotic low-temperature phases of strongly correlated systems, including the antiferromagnetic insulating and unconventional superconducting phases of the high T_c cuprates [1], the charge-ordered insulating and ferromagnetic metal phases of the manganites [2], the orbital-ordered and ferromagnetic metal phases of the ruthenates [3–5], and the charge-density-wave (CDW) and superconducting phases of layered dichalcogenides such as 2H-$NbSe_2$ [6]. Of particular interest is the exotic phase behavior that is expected between fully ordered (crystalline) and disordered (isotropic) phases as one tunes the interactions in these systems using some control parameter other than temperature. These include electronically phase-separated regimes [2], and "quantum liquid crystal" phases, which are expected to be observed between charge-ordered insulating and "disordered" metallic or superconducting phases as one increases the interactions between the charge stripes [7]. Clearly, therefore, it is of great interest to carefully explore the manner in which 2D and 3D quantum ordered phases collapse, or "melt," into quantum disordered phases as a function of some control parameter — such as pressure — that tunes the competing interactions in the material at low temperatures.

In this Letter, we report a pressure-dependent low-temperature Raman scattering study of the CDW system 1T-$TiSe_2$, in which we are able to explore the manner in which a quasi-2D CDW state melts with increasing pressure near $T \sim 0$ K. Because of its layered structure and simple commensurate CDW phase, 1T-$TiSe_2$ is an ideal system for such an investigation. 1T-$TiSe_2$ is also of interest because the CDW transition is not driven by conventional Fermi surface nesting, but rather by an unconventional mechanism involving electron-hole coupling and an "indirect" Jahn-Teller effect [8]. Our pressure-dependent light scattering approach allows us to explore unique details associated with quantum mechanical melting of the CDW in 1T-$TiSe_2$. In particular, this study reveals that the CDW state evolves with increasing pressure in a manner reminiscent of classical 2D melting, with crystalline and disordered CDW regimes, as well as an intermediate "soft" CDW regime in which the CDW exhibits strong fluctuations and loses its stiffness.

The 1T-$TiSe_2$ samples used in this study were grown by iodine vapor transport with a temperature gradient of 570–640 °C [8]. The sample stoichiometry was verified by x-ray and resistivity measurements. The Raman spectra were taken in a true backscattering geometry with 647.1 nm incident photons. Variable low-temperature, high-pressure measurements were obtained with a modified SiC-anvil cell inserted into a flow-through helium cryostat, allowing continuous adjustment of both the temperature (3.5–300 K) and pressure (0–100 kbar) [5]. Argon was used as the pressure transmitting medium, and the pressure inside the cell was determined from the shift of the ruby fluorescence line; argon is quasihydrostatic in the temperature and pressure range of interest [9].

Figure 1 shows the temperature-dependent Raman scattering spectrum below the CDW transition temperature at $T_C \sim 200$ K. Several new modes develop in the CDW phase. Of particular interest are an E_g mode near 75 cm^{-1} and an A_{1g} mode near 115 cm^{-1}. These two modes are CDW-coupled "amplitude" modes associated with the zone-boundary transverse acoustic phonons from the L point in the Brillouin zone, which are folded to the zone center due to the formation of the CDW superlattice [10,11]. That these two modes are indeed coupled to the CDW mode is confirmed by their temperature dependence in Fig. 2: Both the 75 cm^{-1} E_g and 115 cm^{-1} A_{1g} amplitude mode energies soften dramatically as the temperature is increased toward the CDW transition temperature. By contrast, the 134 cm^{-1} E_g and 203 cm^{-1} A_{1g} zone-center optical phonon energies are nearly temperature independent, indicating that they are not strongly influenced by the development of the CDW state.

The CDW amplitude modes are excitations of the CDW ground state, involving fluctuations of the CDW state that modulate the amplitude of the charge-density wave. In particular, the A_{1g} amplitude mode near

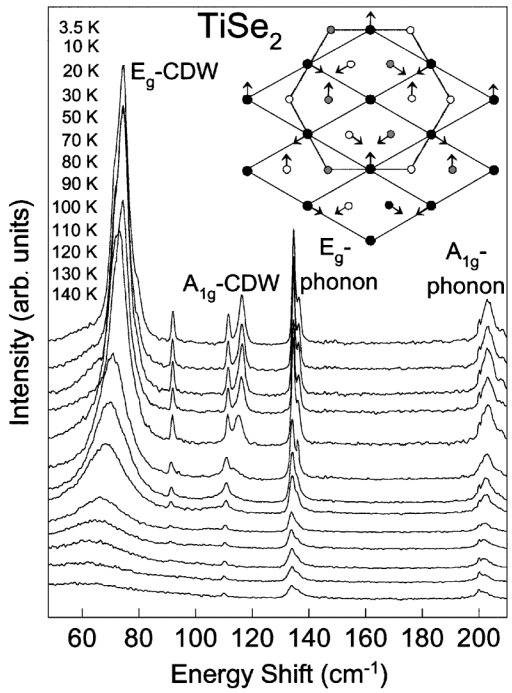

FIG. 1. Temperature dependent Raman scattering spectra of $TiSe_2$. The inset shows the displacement pattern associated with the CDW distortion, for Ti atoms (solid circles), Se atoms above a Ti layer (open circles), and Se atoms below a Ti layer (shaded circles).

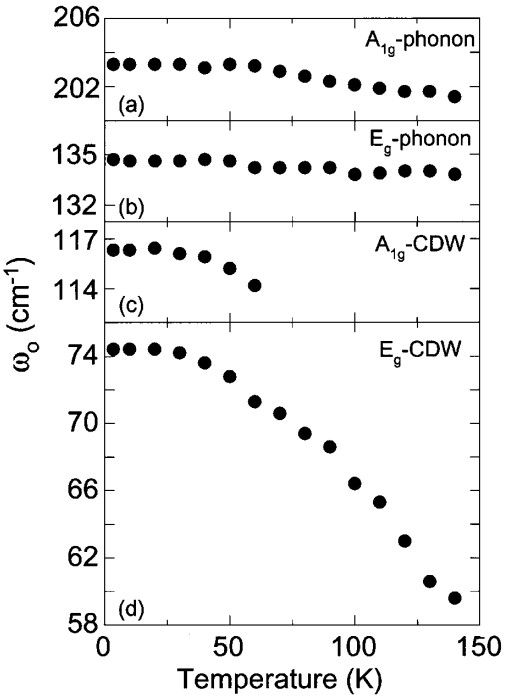

FIG. 2. Temperature dependence of the peak energies of (a) the A_{1g} optical mode, (b) the E_g optical mode, (c) the A_{1g} CDW mode, and (d) the E_g CDW mode.

115 cm^{-1} involves fluctuations of the CDW amplitude that preserve the symmetry of the CDW ground state (Fig. 1 inset), while the E_g amplitude mode involves out-of-phase fluctuations of the CDW amplitude away from the ground state symmetry. These two amplitude modes serve as ideal "probes" with which to study the stability and stiffness of the CDW state as it evolves and melts as a function of increasing pressure.

Figure 3 shows the pressure-dependent Raman spectra of $TiSe_2$ at 3.5 K. The energy and intensity of the 115 cm^{-1} A_{1g} and 75 cm^{-1} E_g CDW amplitude modes, along with both the 134 cm^{-1} E_g and 203 cm^{-1} A_{1g} optical phonon modes, are summarized in Fig. 4. One of the chief effects of pressure on the low-temperature Raman spectrum of 1T-$TiSe_2$ is the gradual suppression of the 75 and 115 cm^{-1} CDW amplitude mode intensities with increasing pressure, and the complete collapse of the CDW state near a $T \sim 0$ critical pressure of approximately $P^* \sim 25$ kbar. Notably, the dramatic increase in the A_{1g} optical phonon linewidth near $P^* \sim 25$ kbar [Fig. 3(c) inset] betrays increased damping of this phonon by free carriers, indicative of a pressure-induced CDW-metal transition near P^*. This value of the critical pressure is similar to that observed in pressure-induced CDW-to-metal transitions in $NbSe_3$ ($P^* \sim 24$ kbar) [12] and $Lu_5Ir_4Si_{10}$ ($P^* \sim 21$ kbar) [13].

More interesting than the pressure-induced collapse of the CDW phase is the manner in which this collapse occurs. This process can be carefully studied by examining the energies and intensities of the 75 cm^{-1} E_g and 115 cm^{-1} A_{1g} amplitude modes as a function of pressure, summarized in Figs. 4(c) and 4(d), respectively. For comparison, Fig. 4 also summarizes the pressure-dependent energies of both the (a) 203 cm^{-1} optical phonon and (b) 134 cm^{-1} optical phonon modes.

Notably, Fig. 4 reveals several regimes of behavior associated with the pressure-induced ($T \sim 0$) quantum melting of the CDW state in 1T-$TiSe_2$:

(i) *Crystalline CDW regime.*—From $P = 0$ to 5 kbar, the A_{1g} CDW amplitude mode's intensity decreases slightly, but its energy increases at a rate of approximately $d\omega_o/dP \sim +1$ cm^{-1}/kbar. This behavior is consistent with increased stiffening of the CDW state with increased pressure, indicative of a "crystalline" regime. Significantly, the manner in which the A_{1g} amplitude mode energy increases with pressure is similar to that of the 203 cm^{-1} [Fig. 4(a)] and 134 cm^{-1} [Fig. 4(b)] optical modes, providing evidence that the CDW remains commensurate with the lattice in this regime.

(ii) *Soft CDW regime.*—Between roughly $P \sim 5$ to 25 kbar, the A_{1g} amplitude mode exhibits a number of interesting and anomalous changes as a function of increasing pressure: its energy softens—revealing an anomalous, slightly negative Grüneisen mode parameter $d\omega_o/dP$ in this regime [14]—its intensity decreases rapidly, and its linewidth increases substantially [Fig. 3(c) inset]. By contrast, neither the 134 cm^{-1} E_g nor the 203 cm^{-1} A_{1g} optical phonon modes show an appreciable

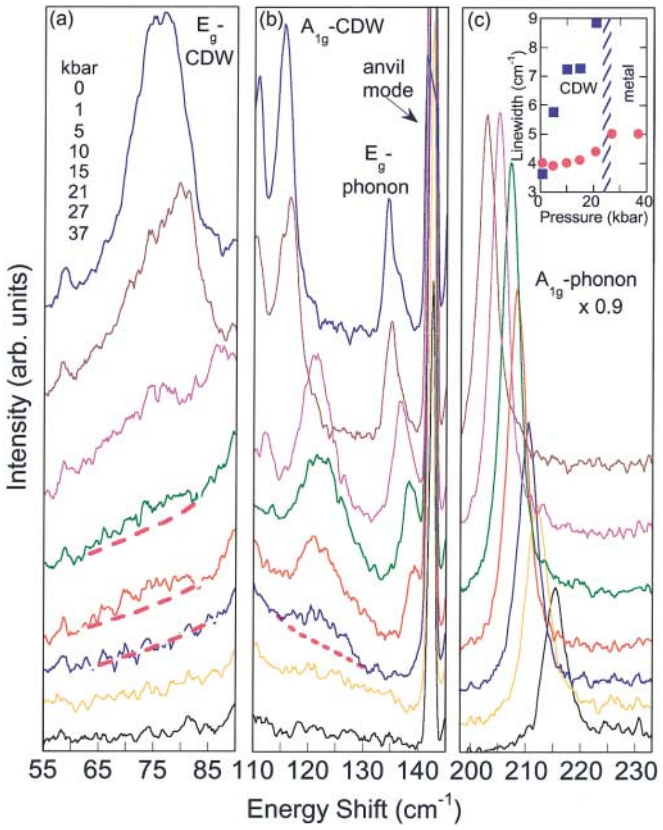

FIG. 3 (color). Pressure dependence of the Raman spectra of $TiSe_2$ at $T = 3.5$ K for (a) the E_g CDW mode, (b) the A_{1g} CDW and E_g optical phonon modes, and (c) the A_{1g} optical phonon mode ($P = 0$ spectrum not shown for clarity). The intense mode near 143 cm^{-1} in (b) is an anvil phonon mode. The inset shows the pressure dependence of the A_{1g} optical phonon (red circles) and A_{1g} CDW mode (blue squares) linewidths (FWHM).

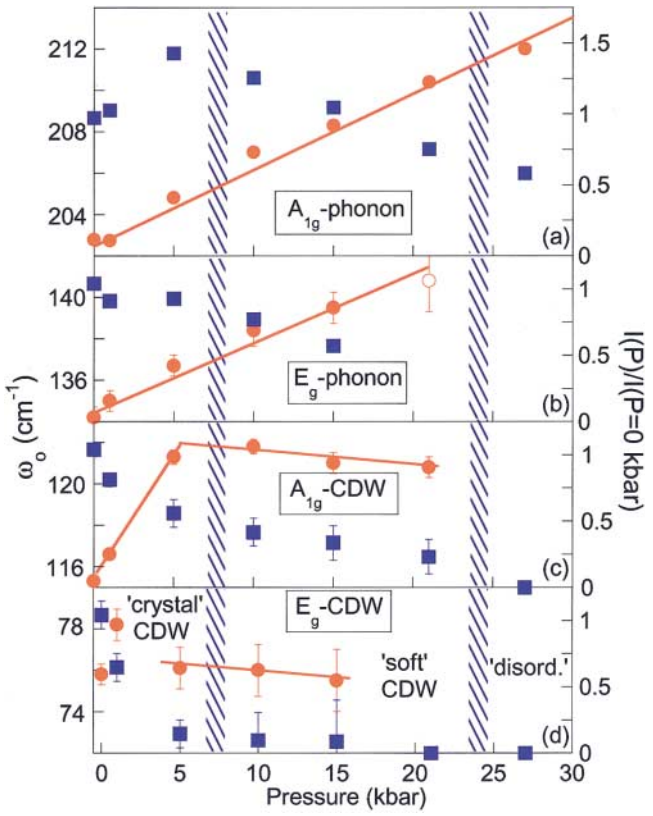

FIG. 4 (color). Pressure dependence of the peak energies (circles) and normalized intensities, $I(P)/I(P = 0)$ (squares) at $T = 3.5$ K for (a) the A_{1g} optical mode, (b) the E_g optical mode, (c) the A_{1g} CDW mode, and (d) the E_g CDW mode. The hatched lines denote rough boundaries between crystalline CDW, soft CDW, and disordered CDW regimes.

change in either intensity or linewidth throughout this pressure regime. The behavior of the A_{1g} CDW mode in this regime is consistent with a distinct softening of the CDW state to breathing-mode fluctuations of the CDW amplitude, and with an increase in CDW fluctuations near P^*. Equally interesting is the fact that the energy of the A_{1g} CDW amplitude mode exhibits a distinctly different pressure dependence than the E_g or A_{1g} optical phonon modes in this regime, suggesting that the CDW becomes incommensurate with the lattice [15,16]. Importantly, the E_g amplitude mode also exhibits a particularly anomalous pressure dependence in this regime, including a decrease in energy and a rapid reduction in intensity with increasing pressure. The rapid disappearance of the E_g mode, in particular, indicates that out-of-phase fluctuations of the CDW amplitude are not well-defined excitations above roughly $P \sim 5$ kbar, even though there is clearly some vestige of the A_{1g} CDW mode at these pressures. This may indicate a breakdown of long-range CDW order in this phase regime; indeed, calculations of 1D CDW systems show that a softening of the CDW to shear deformations, and a consequent breakdown of long-range translational order, occurs when the coupling between CDW stripes reaches a critical value [17]. In sum, the behavior of the CDW modes in the "soft CDW" regime is characteristic of a regime in which the CDW has begun to soften, or melt, as well as exhibit increasing CDW fluctuations.

(iii) *Disordered CDW regime.*—Finally, above roughly $P^* \sim 25$ kbar, both the E_g and A_{1g} CDW amplitude modes are completely suppressed; consequently, there is no evidence in the spectra for long- or short-range CDW order, indicating that the CDW state has melted completely into a metallic or semimetallic phase.

It is interesting to compare the pressure-induced "melting" process described above for $1T$-$TiSe_2$ to melting in other 2D systems [18,19]. Calculations of classical melting in 2D solids suggest the presence of a "hexatic" phase — in which long-range orientational order is preserved, but long-range translational order is lost — intermediate between the crystalline and disordered phases. This topological phase arises because dislocations cause translational order to decay exponentially, but cause a much weaker suppression of orientational order. Such a hexatic-like phase has indeed been observed as a function of increasing disorder (x) in the layered $Nb_xTa_{1-x}S_2$

system using scanning-tunneling microscopy (STM): these measurements reveal a system that is, in turn, crystalline ($0 < x < 0.04$), hexatic ($0.04 \leq x \leq 0.07$), and amorphous ($x > 0.07$), as a function of increasing disorder (x).

While classical melting in 2D systems is reminiscent of the phase behavior we observe as a function of pressure in $1T$-$TiSe_2$, an important qualification should be made with respect to this comparison. In contrast to the examples above, the melting process we observe in $1T$-$TiSe_2$ is quantum mechanical in nature, in that it is driven near $T \sim 0$ K by pressure tuning the competing interactions in this system. To understand the nature of this competition, note first that the zero-pressure CDW state in $1T$-$TiSe_2$ is unconventional, arising from an indirect Jahn-Teller–type interaction that splits and lowers the unoccupied conduction band [8]: as a result of the electron-hole interaction between the conduction and valence bands, the lowering of the split conduction band "repulses" and flattens the valence band, resulting in a lowering of the system's energy, and the formation of a small gap CDW state. Upon applying pressure to this CDW state, one expects several regimes of behavior: at low applied pressures, increasing pressure will increase the matrix element associated with the Jahn-Teller interaction; this is expected to result in a further lowering of the conduction band, and via the electron-hole coupling, to cause a lowering of the valence band and a consequent stiffening of the CDW state. This behavior is similar to that observed in the "crystalline CDW" regime of Fig. 4. As the pressure is increased beyond a critical pressure, however, the increasing strength of the Jahn-Teller interaction is expected to overwhelm the electron-hole interaction between the conduction and valence bands, leading to a collapse of the CDW gap, and a pressure-induced transition to a metallic phase in which the CDW distortion is completely suppressed. Again, the dramatic increase in the linewidth of the A_{1g} optical phonon above P^* [Fig. 3(c) inset], as well as the disappearance of the CDW mode intensities, is indicative of such a pressure-induced metallic phase above P^* in $1T$-$TiSe_2$. Most significantly, our results indicate that, prior to the complete collapse of the CDW gap above P^* in $1T$-$TiSe_2$, there is a distinct soft CDW phase regime in which the CDW loses its stiffness; this appears to result from increased fluctuations of the CDW near P^*, likely caused by an increase in free carriers as the CDW gap collapses. In theoretical support of this, Zaitsev-Zotov *et al.* have shown that increased coupling between CDW stripes leads to an increase in dynamic fluctuations and a decreased CDW stiffness [17]. Interestingly, such long wavelength lattice fluctuations are expected to destroy long-range translational order but preserve long-range orientational order [20].

In summary, Raman scattering studies of $T \sim 0$ pressure-induced melting of the CDW state in $1T$-$TiSe_2$ reveal a low-pressure ($P < 5$ kbar) crystalline CDW regime, a high-pressure ($P > 25$ kbar) metallic regime, and an intermediate pressure regime ($5 < P < 25$ kbar) in which the CDW loses its stiffness, exhibits increased fluctuations, and may have only short-range order. This pressure-induced melting of the CDW state in $1T$-$TiSe_2$ is noticeably different from classical 3D melting, which occurs via an abrupt first-order transition, and instead appears to occur in a manner more akin to classical 2D melting.

We thank E. Dagotto, E. Fradkin, M.V. Klein, and M. Rübhausen for useful discussions. This work was supported by the National Science Foundation under Grant No. DMR-0244502 and by the Department of Energy under Grant No. DEFG02-91ER45439.

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