# Quenching of phase coherence in quasi-one-dimensional ring crystals

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A comparison of the single-particle (SP) dynamics of whisker and ring $NbSe_3$ crystals provides new insight into the phase transition properties of quasi-one-dimensional charge density wave (CDW) systems. In the incommensurate CDW phase, SP relaxation triggered by an ultrafast laser pulse reflects the formation of collective states, and reveals the divergence of the relaxation time when approaching a transition temperature. The degree of divergence is less pronounced in rings than in whiskers, suggesting a loss of phase coherence in ring crystals characterized by a closed-loop topology.

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Over the last few decades, there has been intense interest in understanding the properties of charge density waves (CDW) in quasi-one-dimensional (1D) metals, where one of the most widely discussed issues is the influence of phase fluctuations on CDW transitions.[1] In an uncoupled-1D system, large fluctuations greatly reduce the CDW transition temperature ($T_c$) below the mean-field transition temperature. CDWs undergo a phase transition only when long-range three-dimensional (3D) order develops.[1] Indeed, a pronounced finite size effect has been observed in $NbSe_3$, in which a reduction in the number of parallel chains makes the transitions less pronounced and reduces $T_c$.[2] In this sense, it is also expected that crystal topology will make a substantial contribution to the phase transition since the topology imposes additional constraints on interchain correlations. However, the effects of crystal topology on CDW properties are still poorly understood.

Recently, several 1D transition metal chalcogenides of the type $MX_3$ were found to have various types of topological crystals, where the whisker crystals naturally form ring, Möbius, and figure-of-eight geometries.[3,5] The small sizes and damage-free formations of these structures make it possible for CDWs to maintain their coherence within individual chains with a closed loop, thus making them good candidates for studying the effects of topology on the long-range ordering. In this work, we have investigated topological crystals of $NbSe_3$ by measuring time-resolved optical reflectivity changes. A comparison of the single-particle (SP) decay of whisker and ring structures reveals a significant difference, suggesting that the crystal topology influences their phase transitions.

Figures 1(a) and 1(b) show scanning electron micrographs of a $NbSe_3$ whisker and ring, respectively. Both crystals were prepared by the chemical vapor transport method under virtually the same conditions. The whisker has a standard bulk with a length of a few mm (along the conducting axis $b$) and a width of 50 $\mu$m. The ring has a somewhat different structure with an outer diameter of 50 $\mu$m and an internal diameter of several $\mu$m (conducting axis $b$ in the tangential direction). The circumference of the center hole is around 10 $\mu$m and this is comparable to the correlation length of CDWs ($\xi_{\parallel b} > 2.5$ $\mu$m)[4] in this compound. The details of the growth mechanism for the ring and its structural analysis based on x-ray diffraction have been described in detail elsewhere.[5]

To evaluate the CDW properties, we employed an optical measurement technique that is ideal for observing topological structures since the photon can act as a noncontact probe and therefore preserve the crystal topology. A time-resolved measurement was achieved by using a conventional pump-probe technique with a micro-optical setup. For the excitation source, we used a mode-locked Ti:Sapphire laser with a pulse width of ~130 fs centered at an energy of 1.56 eV with a repetition rate of 76 MHz. We detected the reflectivity change ($\Delta R$) of the probe pulse as a function of the delay

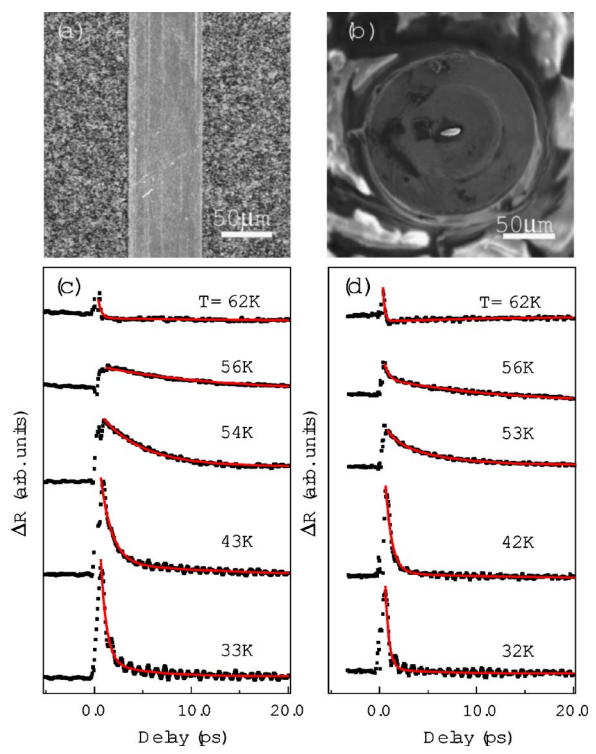


FIG. 1. (Color online). Electron micrographs of the topological samples: (a) Whisker and (b) ring. The corresponding transient reflectivity changes, $\Delta R$, at various temperatures below and above $T_{c2}$ in (c) and (d). The solid lines indicate the results of least-squares fitting.

 

from the pump pulse. The pump and probe pulses were orthogonally polarized and focused through an objective lens onto a single-crystal region. The probe polarization was set along the chain direction of the whisker, where an efficient transient signal was observed. On the other hand, for the ring crytal, we set the probe polarization along any arbitrary axis in the *b*-*c* plane. The pulse overlap had a diameter of 10 $\mu$m on the sample surface. This overlap was monitored using a charge coupled device camera, and was kept at a fixed position during the measurement of each sample. For the ring sample, the position was fixed so that it was near the inner hole in order to emphasize its topological character. The pump and probe fluences were $\sim 40\ \mu\mathrm{J/cm}^2$ and $\sim 10\ \mu\mathrm{J/cm}^2$, respectively. The steady-state heating caused by the laser was accounted for by measuring the excitation-power dependence of $\Delta R$.

$NbSe_3$ consists of three pairs of metallic chains parallel to the conducting axis, and exhibits two incommensurate CDWs with transition temperatures at $T_{c1}=145$ K and $T_{c2}=59$ K. Note that similar $T_c$'s ($T_{c1}=140.8$ K and $T_{c2}=57.4$ K) have been found in ring samples by resistivity measurement.[5] Figures 1(c) and 1(d) show several transient $\Delta R$'s of a whisker and a ring, respectively, for various temperatures below and above $T_{c2}$. As observed in $K_{0.3}MoO_3$ and several other CDW compounds,[6,7] the signal at the lowest temperature is dominated by two features: A combination of exponential responses and damped sinusoidal oscillations. We assign the exponential part to the transient responses of the SPs, while the oscillation part reflects coherent motions—including phonon and collective CDW modes induced by instantaneously photoexcited SPs.

We will now focus our attention on the SP dynamics. The interpretation of the transient $\Delta R$ in CDW systems has been established by analogy to that in widely used materials, such as metals and semiconductors.[6,8,9] Since a pump pulse with near-infrared energy can excite SPs into continuum states far above the CDW gap, relaxation to states near the band edge results in an abrupt increase in $\Delta R$. The CDW gap then causes carriers to accumulate at its upper edge. A subsequent decay thus reflects the transient density change of these accumulated carriers. Since the CDW gap depends on the sample temperature, this fast decay exhibits a temperature dependence associated with the formation of the gap.[6,8] A long-lived decay can be attributed to relaxation from phason states pinned just above the ground state and/or impurity-related trapped states within the gap.[9]

When the temperature is increased to $T_{c2}$, the decay time in both types of crystal increases—followed by an abrupt decrease above $T_{c2}$. The relaxation process across the gap is manifested as phonon emissions and absorptions. Since the energy gap of CDWs is strongly temperature dependent and decreases as it approaches $T_{c2}$ from below, the increase in phonon density—which can contribute to the reabsorption process—results in an increase in the relaxation time. The divergence of the decay time just below $T_{c2}$ thus reflects the formation of a collective gap.

It is important to note that no significant changes occur in $\Delta R$ at around $T_{c1}$ under the present experimental conditions with a probe energy of 1.56 eV. On the other hand, $\Delta R$ with a probe energy of 1.1 eV shows characteristically diverse behavior at each transition temperature. In the latter case, however, the SP response from another chain can contribute more to the signal below $T_{c2}$ than in the former case. In addition, $T_{c2}$ is suitable for analyzing characteristic SP dynamics because the transition at a lower temperature reduces the thermal fluctuation and makes the collective gap formation clearer than that at a higher temperature.

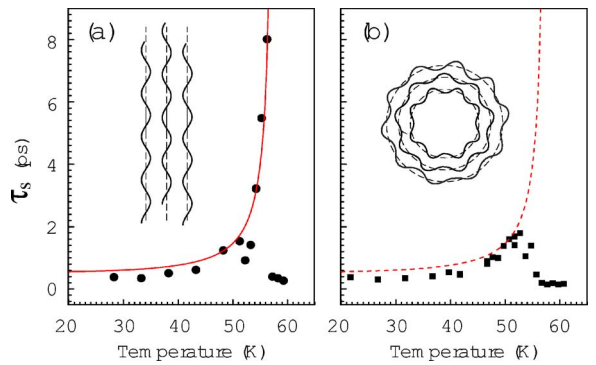


FIG. 2. (Color online) Temperature dependences of $\tau_s$ in the whisker (a) and ring (b) around $T_{c2}$. The solid line in (a) shows a theoretical fit (Ref. 8) to the data, and this is also shown in (b) for comparison, where a large reduction in $\tau_s$ and disagreement with the theoretical curve are clearly seen. Insets: Sketches of CDWs modulated on neighboring chains. Below the mean-field temperature, Coulomb repulsion tends to align the CDWs out of phase with each other.

Figures 2(a) and 2(b) show plots of the fast decay time ($\tau_s$) as a function of temperature in the whisker and ring, respectively. In accordance with the SP relaxation processes described above, we evaluated $\tau_s$ by a least-squares fitting procedure with the sum of two exponential functions. Below $\sim 40$ K, $\tau_s$ in both samples is nearly constant ($<1$ ps). In contrast, a clear difference is seen above $T=50$ K, where $\tau_s$ diverges due to the reduction in the gap energy. However, the degrees of divergence of $\tau_s$ are very different in these two samples. For a better comparison, Fig. 3 shows simultaneous plots of transient signals associated with the longest decay time. The signal in the whisker exhibits an extremely long exponential decay whose evaluated $\tau_s$ reaches almost 10 ps. In contrast, $\tau_s$ in the ring is almost 2 ps.

For another qualitative analysis of $\tau_s$, we fit the data in terms of the Bardeen–Cooper–Schrieffer (BCS)-type temperature dependence of the gap $[2\Delta_g(T)]$. The solid curve in Fig. 2(a) represents the theoretical fit given by Kabanov *et al.*[8] to the data with $\Delta_g(0)\approx 50$ meV. Although $2\Delta_g(0)$ in $NbSe_3$ obtained in previous experiments varies significantly,[10] $\Delta_g(0)\approx 50$ meV obtained in our optical measurement is in good agreement with the maximum gap value of $45\pm 10$ meV obtained with angle-resolved photoemission spectroscopy.[11] On the other hand, we cannot accurately fix the parameter using the ring data. This is due to the quenching behavior of $\tau_s$ at around $T_{c2}$. Instead, the curve optimized for the whisker is represented by the dashed line in Fig. 2(b). A marked deviation from the theoretical fit can be seen in the vicinity of $T_{c2}$. This discrepancy suggests that the transient $\Delta R$ reflects the critical Ginzburg–Landau fluctuations, where $\Delta_g(T)$ cannot be reproduced by conventionally used

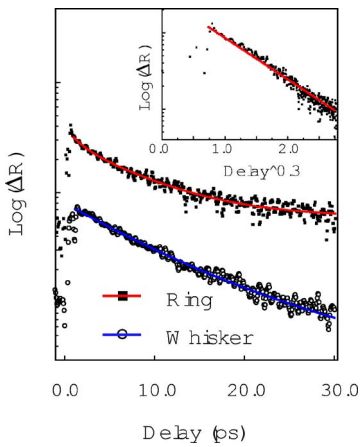


FIG. 3. (Color online) Semilogarithmic plots of the reflectivity changes for the whisker ($T$=56 K) and the ring ($T$=52 K), where the longest $\tau_s$ was obtained in each crystal. The plots are shifted vertically for clarity. The inset shows another plot for the ring. The solid line indicates the slope of $\exp(-t/\tau)^{0.3}$, where $\tau$ is 1.61.

theoretical analysis based on the mean-field approximation.

We now consider the topological effect on the phase transition properties on the basis of the different $\tau_s$ temperature dependences of the crystals. The difference in the longest $\tau_s$ at $T_{c2}$ is attributed to the difference between the coherences of the collective states of the samples. In this case, the suppressed divergence of the decay time observed in the ring indicates quenching of the phase coherence. The insets in Figs. 2(a) and 2(b) are schematic illustrations of the candidate spatial distributions of charge density along the individual chains for the whisker and the ring, respectively. Let us recall the phase transition process in CDW materials. In a quasi-1D system, the Coulomb correlation between adjacent chains should be taken into account in the phase transition.[1] In a whisker, 3D ordering can be easily realized by adjusting the neighboring chains with a phase difference of $\pi$. In contrast, for a ring crystal, CDWs with the same oscillation period in the closed loop reduce the Coulomb repulsion solely by undergoing a lattice expansion, resulting in a loss of phase coherence between adjacent chains. This topologically induced phase fluctuation is also consistent with deviations from the BCS-type temperature dependence in the vicinity of $T_{c2}$. The enhanced phase fluctuation prevents the divergence of the relaxation time represented by the mean-field approximation. As a result, the transient $\Delta R$ in the ring renders the critical phase fluctuations clear at around $T_{c2}$. So far, only the size effect has been focused on in discussions of the interchain interaction in quasi-1D systems.[2] However, based on the mechanism discussed above, crystal topology can also enhance the phase fluctuations between neighboring chains.

Note that it is also possible to consider that the difference between the $\Delta R$ values of the two crystals arises from the nonconservative polarization axis characterized by the ring shape. However, as far as the decay constant of $\Delta R$ is concerned, almost no polarization dependence was observed even in the whisker, while the magnitude of $\Delta R$ reveals a strong anisotropy with respect to the conducting axis. Therefore, we conclude that the polarization effect can be excluded

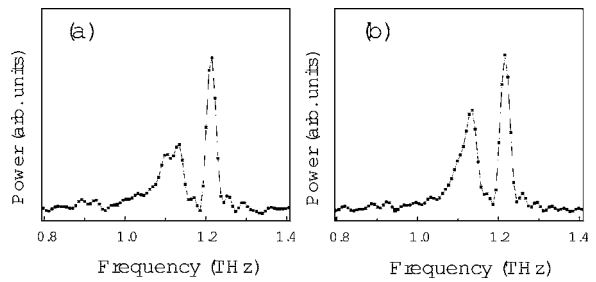


FIG. 4. Fourier transform of the oscillation signal obtained by subtracting the exponential contributions from the data: (a) Spectrum for the whisker at 28 K and (b) spectrum for the ring at 27 K. The peak at the lower frequency is that of an amplitude mode (AM).

from our discussions based on the differences in the decay properties.

We now briefly comment on the relaxation function of the transient $\Delta R$ in the vicinity of $T_{c2}$. Recently, Nogawa *et al.*[12] proposed a phase field model for CDWs in ring crystals remarking on the frustration between intra- and interchain couplings. By using Monte Carlo simulations, they found that the relaxation function in the low-temperature-ordered phase exhibits a power-law decay instead of the usual exponential decay. On the other hand, we should note that the transient $\Delta R$ for the ring is well fitted by a function of $\exp(-t/\tau)^{0.3}$ in comparison with the simple exponential decay for the whisker, as highlighted in Fig. 3.[13] These facts suggest that the type of phase transition for ring-shaped CDWs is essentially different from that for whiskers. In the slow relaxation expressed by a power or stretched exponential function, the enhancement of phase fluctuations originating from the ring topology must play an important role.

Nevertheless, it is also possible to explain the different transient dynamics in terms of the differences between the crystal inhomogeneities of the samples. Since the phase fluctuation is sensitive to impurities, dislocations, and other disorders, we cannot completely exclude the contribution of the crystal inhomogeneities to the present results. As a simple check, we evaluated a coherent oscillation of CDWs induced by instantaneous optical excitation. Since the dephasing time of collective motion is determined by the CDW coherence length, we can qualitatively compare the crystal inhomogeneities.

Figures 4(a) and 4(b) show the fast Fourier transform spectra of the whisker and the ring, respectively, at almost the same temperature. In each spectrum, two distinct peaks are clearly visible. The lower mode at around 1.1 THz shows a softening behavior with increasing temperature and completely disappears above $T_{c2}$, indicating the collective excitation of the CDW (amplitude mode: AM) associated with the incommensurate phase of $T_{c2}$, while the higher mode is identified as a coherent phonon because of its less pronounced temperature dependence. Note that this is the first observation of the AM mode in $NbSe_3$. However, its frequency and temperature dependences are qualitatively similar to the AM oscillation observed in several other CDW compounds.[6,7] The linewidths of the AM obtained from the

Lorentzian fits to the spectra are ~75 GHz for the whisker and ~48 GHz for the ring, which are comparable values. We thus believe that the contributions made by crystal inhomogeneities to the phase fluctuation are almost the same.

In summary, we have investigated the ultrafast SP dynamics in ring and whisker $NbSe_3$ crystals, in terms of the crystal topology. In the phase transition around $T_{c2}$, the temperature dependence of the SP recombination time observed in the ring is quantitatively and qualitatively different from that in the whisker: The divergence of $\tau_s$ is quenched and there is a divergence from BCS-type temperature dependence. These results can be explained in terms of the enhanced phase fluctuation in the closed-loop topology.

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