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Title	Selective optical probing of the charge-density-wave phases in NbSe3
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Citation	Physical Review B, 75(11), 115120 https://doi.org/10.1103/PhysRevB.75.115120
Issue Date	2007-03
Doc URL	http://hdl.handle.net/2115/22082
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Type	article
File Information	PRB75-11.pdf

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Selective optical probing of the charge-density-wave phases in NbSe₃

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(Received 27 October 2006; published 21 March 2007)

We report a study of the ultrafast single particle dynamics in quasi-one-dimensional NbSe₃ whisker crystals using a two-color pump-probe measurement. A selective enhancement of the relaxation dynamics connected with one of the two charge-density-wave (CDW) phases was realized by tuning the probe energy to around 1.5 eV, in which the temperature dependence across the corresponding phase transition shows a pronounced anomaly. A similar selective excitation was possible in the coherent CDW oscillation.

I. INTRODUCTION

Photoinduced absorption and/or reflection spectroscopy using ultrafast laser pulses has become a powerful tool for studying the excitation dynamics of phase transition materials.[1–5] Here, the time-resolved data allows us to follow the nonequilibrium single-particle (SP) and collective electron dynamics that are inaccessible with other conventional techniques. Recently, this optical technique was applied to materials characterized by the coexistence of multiple phases,[1–3] which involves interesting phenomena such as high-T_C superconductivity and quantum fluctuation effects. However, in this case, the transient signal becomes complicated by a superposition of relaxation components derived from the individual phases. Therefore, the selective probing of individual phases is essential if we are to obtain precise measurements.

In this paper, we demonstrate that the phase-selective measurement of NbSe₃ crystals is possible by using a two-color optical pump-probe measurement, which allows us to evaluate the photoexcited SP dynamics precisely even in coincidence with different phases. The temperature dependence of the transient data shows a dramatic change in its amplitude and decay time across T_C. The magnitude of these changes strongly depends on the probing energy, which allows the selective enhancement of the signal of the corresponding charge-density-wave (CDW) phase.

II. EXPERIMENT

The samples studied in the present work are NbSe₃ whisker-shaped single crystals with lengths of a few mm along the conducting axis and widths of ~50 μm. They were synthesized by the chemical vapor transport method. NbSe₃ is the most extensively studied quasi-one-dimensional (1D) CDW compound.[6,7] This compound undergoes two independent Peierls transitions to CDW phases at T_{C1}=145 K and T_{C2}=59 K. These two CDWs occur on two of three types of chains with different nesting conditions in **k** space. The other chains remain metallic down to the lowest temperatures. Therefore NbSe₃ is regarded as a multiple phase system.

Previous pump-probe measurements were performed with a conventional lens, and by restricting the CDW compounds to those with a large single-domain size. Here, we employed a two-color pump and probe setup with an objective lens, in which the coaxial configuration between the pump and probe beams increases the spatial resolution up to the diffraction limit, and allows reflectivity changes with a high signal to noise ratio even in the thin whisker samples.

Time-resolved data for the photoinduced dynamics of CDWs serve as snapshots of reflectivity changes (ΔR). For the excitation source, we used an optical parametric oscillator (OPO) pumped by a mode-locked Ti:sapphire laser (76 MHz repetition rate). The time resolution was estimated to be around 200 fs from cross correlation measurements. The probe energy can be set from 1.39 to 1.77 eV by using a fundamental pulse and from 1.00 to 1.16 eV by using the OPO. Note that these excitation energies are far greater than the CDW gaps [typically around several tens of meV (Refs. 8 and 9)]. Depending on the experimental configuration, the pump and probe beams can be generated by either the Ti:sapphire laser or the OPO. The pump and probe pulse polarizations were parallel to the conducting axis because ΔR is dominant in this direction, and the pulses were focused through an objective lens onto a single-crystal region. The pump and probe fluences were ~40 and ~10 μJ/cm², respectively. The pulse overlap with a diameter of 10 μm on the sample surface was monitored using a charge coupled device camera, and was kept at a fixed position during the measurements. The steady state heating caused by the laser was accounted for by measuring the excitation power dependence. The sample was mounted on a helium-flow cryostat.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show two typical examples of transient ΔR obtained at probe energies of 1.56 and 1.07 eV, respectively. Both sets of data are strongly temperature dependent, and are qualitatively consistent with previous measurements for similar quasi-1D compounds,[10] in which the transient ΔR observed at temperatures well below T_C consists of two components: one is exponential decay, which predominantly reflects the photoexcited SP dynamics, and the other is coherent collective oscillations. We focus first on the former component.

Since the pump pulse at near-infrared energy can excite the SPs into higher-energy states far above the CDW gap, a quick relaxation to states near the band edge results in an
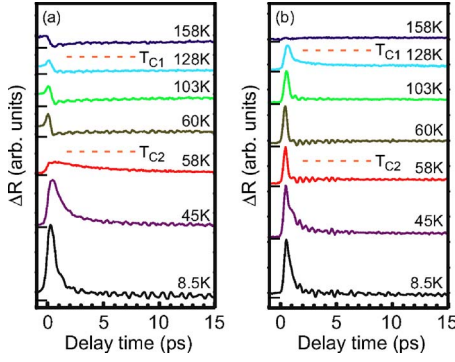
FIG. 1. (Color online) The time-resolved reflectivity change ΔR at various temperatures observed in the two-color pump-probe measurement. The pump and probe energies are, respectively, 1.07 eV and 1.56 eV in (a) and the reverse in (b).

FIG. 2. (Color online) Temperature dependence of τ_{eff} (upper) and S_{eff} (lower) obtained at probe energies of (a) 1.56 eV and (b) 1.07 eV. The solid line in τ_{eff} shows a theoretical fit to the data, and the lines in S_{eff} is a guide for the eye. The inset represents the expanded view of τ_{eff} around T_{C1}.

abrupt change of ΔR. The subsequent exponential decay reflects the transient density change of the SPs accumulated in the vicinity of the gap. When approaching T_C's from below, this component shows an extended decay time with a lower amplitude. This is known as precursor behavior related to gap closing, which occurs due to the efficient reabsorption of nonequilibrium phonons across the gap.[11] Above T_{C1}, i.e., above the temperature at which all chains are metallic, ΔR becomes very small, thus suggesting that the metallic chain contributions are negligible. When we consider the SP relaxation process in each CDW phase separately, the transient ΔR in NbSe$_3$ is described by

$$\Delta R(t, T, \omega_{pr}) \propto \begin{cases} S_1(T, \omega_{pr})e^{-t/\tau_1(T)} + S_2(T, \omega_{pr})e^{-t/\tau_2(T)} \\ \qquad (T \leq T_{C2}), \\ S_1(T, \omega_{pr})e^{-t/\tau_1(T)} \\ \qquad (T_{C2} < T \leq T_{C1}), \end{cases}$$

(1)

where S_n and τ_n are the amplitudes and the relaxation times of the SP component, respectively, for each CDW phase (n =1 for T_{C1} and n=2 for T_{C2}). Note that the S_n is mainly determined by the optical transition probabilities at the probe energy (ω_{pr}). On the other hand, the pump-induced SPs for above-gap excitation average their distribution over the near-gap states during the instantaneous relaxation, resulting in a minor contribution to S_n. In addition, we mainly focus on the fraction of magnitude S_n/S_m ($n \neq m$). In this case, the effect of the number of SPs, which is slightly changed in accordance with the pump energy, is cancelled out. Indeed, we found that the outline of the transient ΔR of the 1.07/1.56 eV (pump-probe) excitation was almost identical to the results for 1.56/1.56 eV (not shown). Therefore we define the characteristic amplitude as a function of ω_{pr}.

The two data sets in Fig. 1 show qualitatively the same temperature dependence but differ quantitatively. In particular, in the temperature range just below T_{C2} where the T_{C1} and T_{C2} phases coexist, ΔR in (a) has a much longer decay time and a larger amplitude reduction than ΔR in (b). These observations indicate that we can selectively probe the pho-
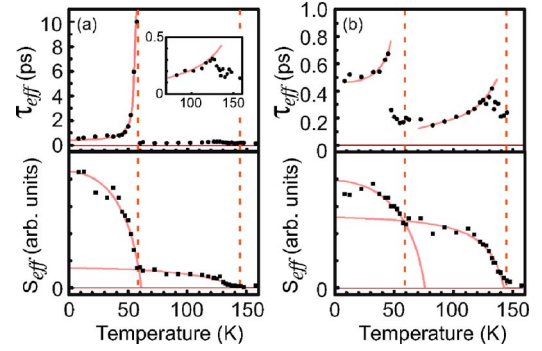
toexcited SP dynamics in the T_{C2} phase as described in detail below.

In Fig. 2, we plot the effective decay time (τ_{eff}) and the amplitude (S_{eff}) at probe energies of (a) 1.56 eV and (b) 1.07 eV, in which we have fitted the exponential function to the data without distinguishing the components given in Eq. (1). In the T_{C2} to T_{C1} temperature range, where S_{eff} and τ_{eff} are actually identical to S_1 and τ_1, respectively, the results show similar temperature dependences for (a) and (b) [compare the inset of (a) with (b)]. As the temperature approaches T_{C1} from below, $S_1(T)$ decreases suddenly and $\tau_1(T)$ increases divergently, suggesting a reduction in the gap energy of the T_{C1} phase. In contrast, below T_{C2}, there is a significant difference between (a) and (b). S_{eff} in (a) shows a great reduction at T_{C2} and its magnitude is 5 times greater than that at T_{C1}, while the magnitudes of T_{C1} and T_{C2} in (b) are almost identical. Correspondingly, one can see that τ_{eff} in (a) diverges up to almost 10 ps around T_{C2} while τ_{eff} in (b) reaches only 1 ps. These results clearly indicate that $S_2 \gg S_1$ is achieved in (a) while $S_2 \approx S_1$ in (b). Therefore $\Delta R(t)$ is approximately described by $S_2(T)e^{-t/\tau_2(T)}$ at ω_{pr}=1.56 eV. Note that at ω_{pr}=1.07 eV, where $\Delta R(t) \propto S_1(T)e^{-t/\tau_1(T)} + S_2(T)e^{-t/\tau_2(T)}$, the divergence of τ_{eff} can be assumed to be due to the relatively large $S_1(T)$ contribution around T_{C2}. In other words, the strong divergence of τ_{eff} observed at ω_{pr}=1.56 eV reflects $\tau_2(T)$ more precisely. Also note that the degree of divergence $\tau_1(T \approx T_{C1})$ is much smaller than that of $\tau_2(T \approx T_{C2})$, which will be discussed later.

To clarify the energy dependence of the selectivity on the SP dynamics in the T_{C2} phase, Fig. 3(a) shows a series of transient ΔR obtained at a temperature just below T_{C2}, where τ_2 exhibits an extended decay. Because we used an OPO as the incident light source, the pump energy is also changed by tuning the probe energy, which may modify the number of photoexcited SPs. To compensate for this effect, we compare τ_{eff} rather than S_{eff} in Fig. 3(b). This figure indicates that the longer τ_{eff} becomes, the more S_{eff} includes the contribution of the T_{C2} phase. The spectrum shows a slowly varying distribution, suggesting the energy dependent enhancement of the contribution of the T_{C2} phase. The maximum value of τ_{eff} is located at ω_{pr}=1.56 eV. Thus we conclude that selective
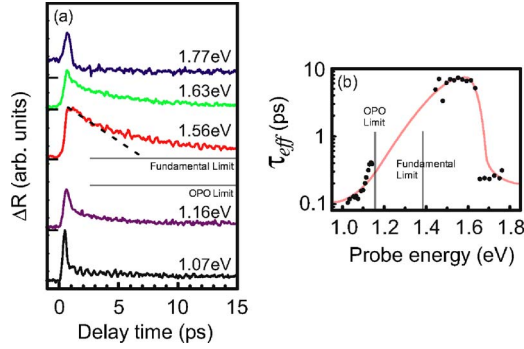
FIG. 3. (Color online) (a) The transient ΔR at various probe energies measured at 58 K. The fundamental and OPO excitation limits are between 1.16 and 1.39 eV. The dotted line shows the longest fast decay component observed at a probe energy of 1.56 eV. (b) Semilogarithmic plots of τ_{eff} as a function of probe energy. The solid line is a guide for the eye.

probing of the T_{C2} phase is achieved in this energy region.

Let us discuss the degree of divergence of τ_n in each CDW phase. On the basis of the theoretical framework developed by Kabanov *et al.*,[11] the SP dynamics reflects the Bardeen-Cooper-Schrieffer (BCS)-type temperature dependence of the gap $[\Delta_g(T)]$. In the simplest approximation, the model yields a τ_n value that is proportional to the inverse of $\Delta_{gn}(T)$. In this case, τ_n diverges to infinity when the temperature is increased close to T_{Cn}. In a real system, τ_n is saturated by the thermal-phase fluctuations. The effects of thermal fluctuation are marginal since here we studied the SP relaxation on a picosecond time scale. The difference in the maximum value of τ_n in the T_{C1} and T_{C2} phases can therefore be explained by the difference in phase fluctuations at T_{Cn}. In this case, the suppressed (enhanced) divergence of τ_1 (τ_2) indicates the suppressed (enhanced) phase coherence for three-dimensional (3D) CDW ordering, which is consistent with the difference in the modulation wave vectors, namely $\mathbf{Q_1}=(0,0.241,0)$ for the T_{C1} phase and $\mathbf{Q_2}=(0.5,0.260,0.5)$ for the T_{C2} phase. We note that the maximum of τ_1 is comparable with the results obtained for the other CDW compounds: τ_{eff} in $1T$-TaS$_2$ and $2H$-TaSe$_2$ reaches only 1 ps (T_C=170 K) and 0.4 ps (T_C=140 K), respectively, and K$_{0.3}$MoO$_3$ reaches almost 1 ps at T_C=180 K. Therefore it is possible to consider that the divergence of τ_2 is extremely large. One possibility for such an enhancement of the maximum τ_2 is the phase locking of the coexisting CDWs below T_{C2}, which has been predicted for the zero-modulation wave vectors in the superposition of two CDWs.[12]

Although these explanations are still speculative, we emphasize that the considerable difference in τ_n indicates a strong sensitivity to the phase transition properties and thus provides a useful parameter for investigating the dynamics and interactions of coexisting CDWs. In this sense, our results connect with recent reports on the sliding properties of NbSe$_3$ CDWs.[13,14] Indeed, a motional 1D coherence accompanied by a loss of transverse correlation above T_{C2} and a sliding induced decoupling of coexisting CDWs have been observed, both of which are consistent with our results.
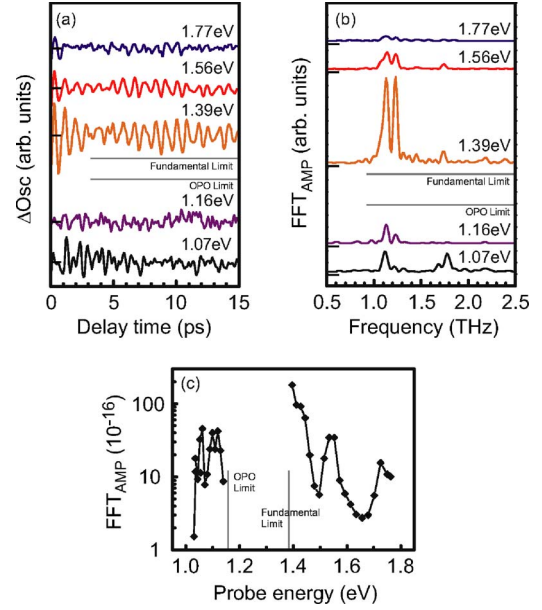

FIG. 4. (Color online) (a) The oscillation transient signal ΔR after subtraction of the decay components at various probe energies obtained at 8.5 K. (b) The FFT spectra of their signals. (c) Semilogarithmic plots of the FFT amplitude of AM (the lower peak at 1.13 THz) as a function of probe energy. The fundamental and OPO excitation limits are between 1.16 and 1.39 eV.

We note a difference in the τ_{eff} saturation behavior was also found in a comparison of topological NbSe$_3$ crystals, where the divergence of τ_2 in the ring NbSe$_3$ is clearly suppressed even in the vicinity of T_{C2}. In accordance with the power-law decay of the transient ΔR around T_{C2}, we have concluded that the results can be explained in terms of the phase fluctuation enhanced by closed-loop topology.[3,15,16]

We now investigate the selectivity of the T_{C2} phase in the lowest temperature regime ($T \ll T_{C2}$). For this purpose, we consider the coherent oscillation part of ΔR, in which one of the CDW oscillations (amplitude mode, AM) clearly exhibits energy dependence. Since coherent AM oscillations are directly connected with optical transitions involving the CDW gap states, the excitation energy dependence of the AM allows us to evaluate the corresponding CDW phase separately.

Figure 4(a) shows a series of such oscillating data at various probe energies after subtraction of the exponential decay. For clarity, the corresponding fast Fourier transform (FFT) spectra are shown in Fig. 4(b). Two characteristic peaks are dominant in these spectra. The lower peak at 1.13 THz shows a softening behavior with increasing temperature and completely disappears above T_{C2}, indicating AM associated with the T_{C2} phase. The higher peak at 1.22 THz is identified as a coherent phonon because of its less pronounced temperature dependence.

It is important to note that at $T \ll T_{Cn}$, the SP dynamics from each CDW phase exhibit almost the same decay time ($\tau_1 \approx \tau_2$) mainly due to the completion of the CDW gap (see the bottom two curves in Fig. 1). Consequently, we cannot distinguish the contributions of the different T_{Cn} phases in the exponential part of ΔR. On the other hand, the AM os-

cillation shows a significant energy dependence as shown in Fig. 4(b). Therefore we consider the AM oscillation amplitude to be an alternative parameter with which to evaluate the contribution of the T_{C2} phase at $T \ll T_{C2}$.

Figure 4(c) shows plots of the FFT amplitude of AM as a function of probe energy. In this case, the more intense the AM is, the more the signal includes the contribution of the T_{C2} phase. As seen in Fig. 4(b), the spectrum exhibits a distribution, where AM becomes dominant by tuning the probe energy to the lower limit of the laser, suggesting an energy dependent contribution of the T_{C2} phase.

We now discuss the mechanism by which the selective excitation for one of two CDW phases was achieved in the transient reflectivity measurements. Previous optical experiments on the NbSe$_3$ whisker have shown that there are several small but distinct resonances originating from interband transitions above the plasma edge.[17–20] Theoretically, the band electronic structure based on tight-binding calculations also predicts the number of higher excited states with flat dispersions parallel to the CDW band where we can expect a large transition probability for the resonant optical excitation.[21,22] As mentioned by Demsar *et al.*,[1] the probe signal for above-gap excitation reflects the interband transitions from the band edge to an appropriate higher excited band. Therefore, the excitation energy dependence in our present results suggests a transition to the excited state with a large transition probability that increases the contribution of the corresponding CDW phase in the signal [see Fig. 5(a)].

We comment on the difference between the resonance energies in the two experiments at different temperatures. Although the exact spectrum peak is obscured by the laser limit in Fig. 4(b), the energy corresponding to the efficient CDW oscillation shifts toward a lower energy than the SP decay spectrum [Fig. 3(b)]. This shift can be explained by the transition schemes summarized in Figs. 5(a) and 5(b). The SP decay was evaluated just below T_{C2}, at which we observed the opening of $2\Delta_{g2}$. On the other hand, we obtained the CDW oscillation at the lowest temperature where the complete gap exists. When we consider the transition from the CDW band edge as the dominant process for the probe signal, the resonance energy should be shifted by the amount of gap energy. $2\Delta_{g2}$ is approximately $65–100$ meV,[3,8,9] which is consistent with the difference in the resonance. Note that the probe signal also reflects the upper edge of the occupied electron band. Figure 4(c) also shows a small peak around 1.56 eV, which may account for this resonance condition.
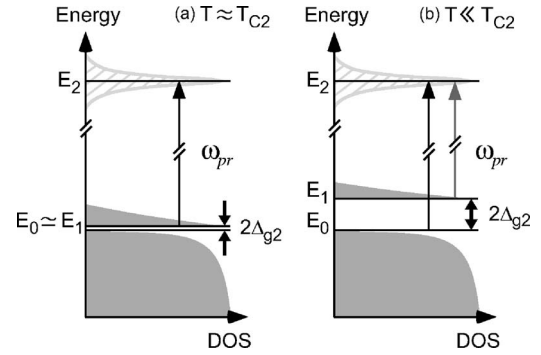

FIG. 5. Schematic diagram of the resonant probe transitions measured in the vicinity of T_{C2} (a) and well below T_{C2} (b). For simplicity, only the transitions from occupied states (E_0 and E_1) to an unoccupied state (E_2) are shown. These two transitions are overlapped in (a).

IV. SUMMARY

In summary, we have performed energy-selective pump-probe reflectivity measurements on whisker NbSe$_3$ with a micron size spatial resolution. The SP dynamics clearly shows two anomalies in the temperature dependence, which reflects the CDW phase transitions. The magnitudes of the anomalies in the SP decay constant and the SP excitation amplitude are changed by changing the excitation energies, indicating selective probing of the CDW phases. We have also demonstrated that the AM oscillation can be employed as another selective probe at the lowest temperature. The results allow us to identify the transient signals in each CDW phase and to clarify the differences in the phase transition properties. In addition, the temperature dependence of selectivity could help to verify the selective excitation mechanism in terms of the optical transitions connected with the CDW gap states. These selective excitation experiments have great potential as regards undertaking precision measurements of nonequilibrium dynamics characterized by the coexistence of multiple phases.

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