Evidence of an Improper Displacive Phase Transition in $Cd_2Re_2O_7$ via Time-Resolved Coherent Phonon Spectroscopy

J. W. Harter,[1,2] D. M. Kennes,[3] H. Chu,[2,4] A. de la Torre,[1,2] Z. Y. Zhao,[5,6] J.-Q. Yan,[5,7] D. G. Mandrus,[5,7] A. J. Millis,[3,8] and D. Hsieh[1,2,*]

[1]*Department of Physics, California Institute of Technology, Pasadena, California 91125, USA*
[2]*Institute for Quantum Information and Matter, California Institute of Technology, Pasadena, California 91125, USA*
[3]*Department of Physics, Columbia University, New York, New York 10027, USA*
[4]*Department of Applied Physics, California Institute of Technology, Pasadena, California 91125, USA*
[5]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[6]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*
[7]*Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA*
[8]*Center for Computational Quantum Physics, The Flatiron Institute, New York, New York 10010, USA*

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We have used a combination of ultrafast coherent phonon spectroscopy, ultrafast thermometry, and time-dependent Landau theory to study the inversion symmetry breaking phase transition at $T_c = 200$ K in the strongly spin-orbit coupled correlated metal $Cd_2Re_2O_7$. We establish that the structural distortion at T_c is a secondary effect through the absence of any softening of its associated phonon mode, which supports a purely electronically driven mechanism. However, the phonon lifetime exhibits an anomalously strong temperature dependence that decreases linearly to zero near T_c. We show that this behavior naturally explains the spurious appearance of phonon softening in previous Raman spectroscopy experiments and should be a prevalent feature of correlated electron systems with linearly coupled order parameters.

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The strongly spin-orbit coupled metallic pyrochlore $Cd_2Re_2O_7$ undergoes an unusual cubic-to-tetragonal phase transition below a critical temperature $T_c = 200$ K that breaks structural inversion symmetry [1]. Unlike many other pyrochlore $5d$ transition metal oxides such as $Cd_2Os_2O_7$ [2] or members of the $R_2Ir_2O_7$ (R = rare earth) family [3], which undergo paramagnetic metal-to-antiferromagnetic insulator transitions below a similar temperature scale, the phase transition in $Cd_2Re_2O_7$ is from metal to metal [4–6] and does not appear to be accompanied by any long-range magnetic order [7–9]. Extensive efforts to determine the underlying mechanism of the phase transition in $Cd_2Re_2O_7$ using x-ray diffraction [1,6,10,11], local magnetic probes [7–9], optical spectroscopy [12–14], and various theoretical approaches [15–18] have produced conflicting pictures.

For many years, the leading hypothesis was that the transition is driven by the freezing of a soft zone-centered phonon mode with E_u symmetry [15]. This mechanism is described by a Landau free energy $F(\Phi) = a(T/T_c - 1)\Phi^2 + b\Phi^4$, where Φ is the structural order parameter, and requires the natural frequency of the E_u phonon to monotonically approach zero near T_c, as illustrated in Fig. 1(a). Such a scenario is supported by Raman spectroscopy experiments [12], which detect the apparent softening of an E_u phonon near T_c, as well as by density functional theory calculations that find an unstable oxygen E_u phonon at zero temperature [16].

A competing hypothesis is that the phase transition is driven by an electronic order. Specific theoretical proposals include an odd-parity electronic nematic order [17,19,20], which arises from a Pomeranchuk instability in the p-wave spin interaction channel [17], as well as a combination of odd-parity quadrupolar and even-parity octupolar magnetic orders [18]. Recent optical second harmonic generation (SHG) measurements have indeed uncovered an odd-parity electronic order parameter Ψ_u with T_{2u} symmetry that

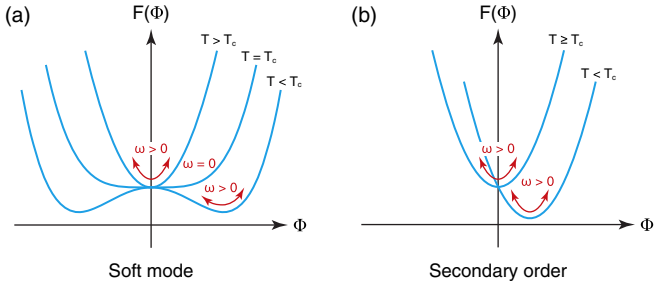

FIG. 1. Two competing hypotheses of the E_u structural distortion in $Cd_2Re_2O_7$ across T_c. (a) The phase transition is driven by the freezing of an E_u phonon. Within this theory, the mode frequency ω softens as $T \to T_c$ and goes to zero at T_c. (b) The E_u structural distortion is a secondary order parameter linearly coupled to the primary electronic order driving the phase transition. Within this theory, the mode frequency does not depend strongly on temperature.

exhibits a $\sqrt{1-T/T_c}$ scaling behavior [14], which is consistent with the behavior of a primary order parameter. Based on a symmetry analysis of the Landau free energy, it was deduced that an additional even-parity electronic order parameter Ψ_g with T_{1g} symmetry must exist, which together with Ψ_u induces the E_u structural distortion as a so-called "improper" secondary order parameter [14]. This mechanism is described by $F(\Phi) = a\Phi^2 - g\Psi_g\Psi_u\Phi$ and does not require the E_u phonon to soften near T_c, as illustrated in Fig. 1(b). The hypothesis of an electronically driven phase transition in $Cd_2Re_2O_7$ is further supported by x-ray diffraction experiments [10], which show an anomalous temperature dependence of superlattice Bragg peaks below T_c, as well as by the extreme weakness of the structural distortion [1,11] contrasted with the pronounced changes in resistivity and magnetic susceptibility [6] across T_c.

To determine which of the two proposed hypotheses is correct and to understand the reasons for conflicting pictures, we carried out time-resolved optical reflectivity measurements on a $Cd_2Re_2O_7$ single crystal to coherently drive the E_u phonon and directly probe its temperature dependence in the time domain. Figure 2(a) shows a characteristic differential reflectivity transient $\Delta R(t)/R$ for $T < T_c$, with t being the delay time between pump and probe pulses. The reflectivity sharply decreases after pump excitation, after which it recovers towards a quasi-steady state less than the initial value. The recovery features oscillations due to the coherent excitation of two Raman-active phonon modes superposed atop a smoothly decaying background. To extract the properties of the modes, we fit the recovery to the function

$$\frac{\Delta R(t)}{R} = B_0 + B_1 e^{-\gamma_1 t} + B_2 e^{-\gamma_2 t} + \sum_{i=1,2} A_i x_i(t), \quad (1)$$

where the two exponential decay terms describe a fast and slow relaxation process and the two damped harmonic oscillator terms describe the phonon modes. We take $x_i(t)$ to be the generic response of an underdamped harmonic oscillator $[\ddot{x}_i + (2/\tau_i)\dot{x}_i + \omega_i^2 x_i = 0]$ with initial conditions $x_i(0) = 1$ and $\dot{x}_i(0) = 0$, given by

$$x_i(t) = e^{-t/\tau_i}\left(\cos(\Omega_i t) + \frac{\sin(\Omega_i t)}{\Omega_i \tau_i}\right), \quad (2)$$

$$\Omega_i = \sqrt{\omega_i^2 - 1/\tau_i^2}. \quad (3)$$

Here, ω_i is the natural frequency of the oscillator, τ_i is its inverse damping parameter, and Ω_i is the actual frequency of damped oscillations. We emphasize the important fact that observing the oscillation frequency approach zero ($\Omega_i \to 0$) does not necessarily imply that the mode is softening ($\omega_i \to 0$). Instead, as we will show, this kind of behavior can also be explained by a diverging damping rate ($\tau_i \to 0$). Indeed, based on the temperature dependence of the raw data alone [Fig. 2(b)], it is clear that the phonon lifetime rapidly diminishes upon approaching T_c.

The values of ω_i and τ_i for the two phonon modes extracted from the fits at different temperatures are displayed in Fig. 3. These best-fit values are uniquely determined because of the exponential decay factor in the oscillator response $x_i(t)$. A number of salient features may be drawn from the results. First, both mode frequencies have a weak temperature dependence and, as illustrated by the gray curve in Fig. 3(a), do not show any signatures of soft mode behavior (where one would expect $\omega_i \to 0$ at T_c). Instead, the observed temperature dependence is fully consistent with a small negative linear slope expected for "normal" phonons [21]. Second, mode 1 only exists below the phase transition whereas mode 2 survives above T_c. Indeed, the frequency and lifetime of mode 1 extracted from our data very closely match a previous Raman study [12] in which the mode symmetry was identified as deriving from an E_u distortion that only becomes Raman active (and therefore experimentally observable) below T_c. In contrast, mode 2 is likely a fully symmetric A_{1g}

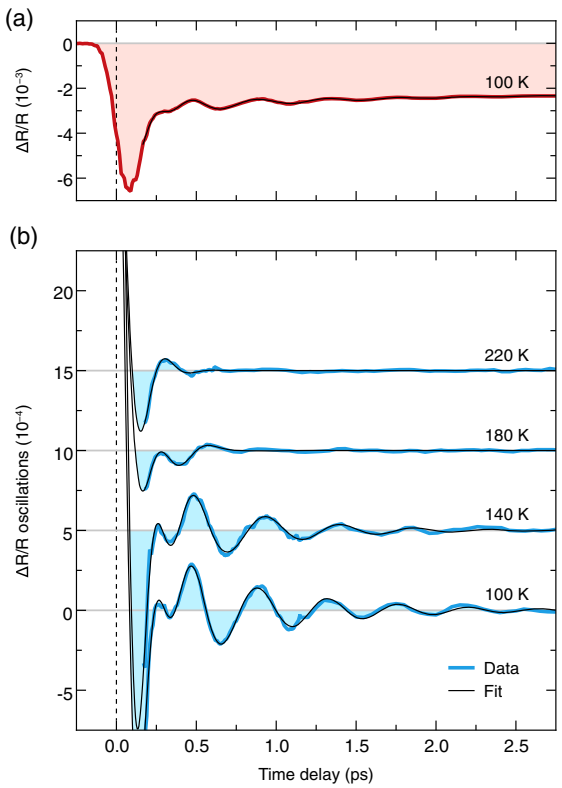

FIG. 2. Time-resolved optical reflectivity of $Cd_2Re_2O_7$. (a) Fractional change in reflectivity $\Delta R/R$ at 100 K as a function of time delay after the pump pulse. (b) Oscillations in $\Delta R/R$ after removal of an exponential background for a selection of temperatures. Curves at different temperatures are vertically offset for clarity, and fits to the data are described in the text. The choice of cosine in the fitting function defines time zero.

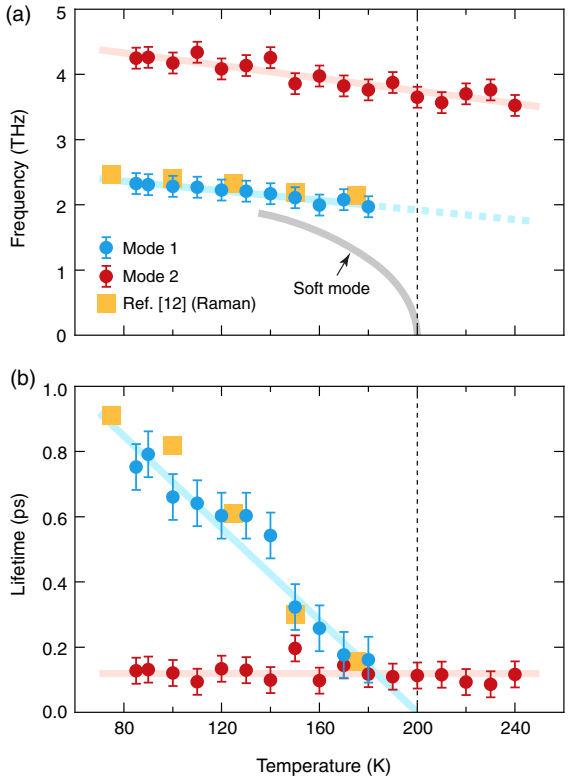

FIG. 3. Phonon mode parameters extracted from the transient reflectivity data. (a) Frequency ($\omega_i/2\pi$) of the two modes. Gray line shows the expected temperature dependence of a soft mode. (b) Lifetime (τ_i) of the two modes. Thick red and blue lines are linear fits to the data. The error bars represent the standard deviation from the linear fits. The statistical errors associated with the fits to Eq. (1) are smaller than the data symbol size. Above 180 K, parameter values for mode 1 could not be reliably extracted from fits due to its short lifetime (see Ref. [22] for details). Our revised analysis of published Raman spectroscopy data [12] is also overlaid for comparison.

breathing mode because it survives above T_c. The absence of mode 2 in the Raman data is possibly the result of its short lifetime and correspondingly broad bandwidth. Third, as shown in Fig. 3(b), the lifetime of mode 1 has a very strong temperature dependence, plunging to nearly zero as the temperature is increased to T_c. The lifetime of mode 2, on the other hand, is relatively short and independent of temperature. These facts strongly disfavor the soft-phonon scenario and suggest that the E_u structural distortion is a secondary order parameter that does not drive the phase transition.

Raman spectroscopy data [12] were originally interpreted as evidence of a softening of the E_u phonon and therefore of a structurally driven phase transition; with our data we see that this interpretation is incorrect. Instead, the reported decrease in the Raman peak frequency near T_c is due to a decrease in the lifetime of the phonon rather than a softening of its natural frequency. This new interpretation is fully consistent with the Raman data if we reanalyze the data using a driven damped harmonic oscillator model [22], where the frequency of the resulting Raman peak does not necessarily correspond to the oscillator natural frequency—a phenomenon well established in the literature [25,26]. As shown in Fig. 3, the values of ω_1 and τ_1 extracted from this revised analysis of the Raman data fully agree with our time-domain analysis, offering an independent consistency check of our results.

Although nontrivial temperature dependencies of mode lifetimes near phase transitions are well established for primary order parameters [27–31], it is unusual to observe such behavior for a secondary order parameter. To examine why the lifetime of the E_u phonon mode has such a strong temperature dependence near T_c despite it not going soft, we analyzed the interaction between the primary and secondary modes in $Cd_2Re_2O_7$ by performing a time-dependent Landau theory analysis of its full free energy proposed by Ref. [14]:

$$F = F_0 - \frac{a}{2}\left(1 - \frac{T}{T_c}\right)(\Psi_u^2 + \Psi_g^2) + \frac{b}{2}\Phi^2 - g\Psi_g\Psi_u\Phi + \frac{c}{4}(\Psi_g^4 + \Psi_u^4). \quad (4)$$

By expanding F about the equilibrium values of the structural (Φ) and electronic ($\Psi_{u,g}$) order parameters and considering the linearized dynamical response to deviations from the equilibrium values, which is valid at temperatures sufficiently below T_c where critical fluctuations are irrelevant, our calculations show that there exists a linear coupling between the primary and secondary modes [22]. This coupling allows the Φ mode to be damped by the critical slowing-down of the $\Psi_{u,g}$ modes. Assuming overdamped dynamics for the $\Psi_{u,g}$ modes and oscillatory dynamics for the Φ mode, our theory produces a Φ mode lifetime $\tau \propto 1 - T/T_c$ in agreement with our measurements. Figure 4 shows the calculated temperature dependence of τ for various values of the coupling strength $\lambda = g^2/bc$ using the experimentally determined phonon natural frequency (2.5 THz). We see that the linear temperature scaling relation is a robust feature of our theory and, for suitably chosen values of the model parameters, can quantitatively reproduce the experimental data.

It is surprising that the data are so well captured by time-dependent Landau theory because an ultrafast optical pulse typically excites the system far away from equilibrium on short time scales, during which the electronic and lattice temperatures can be very different. To measure how quickly the electron and lattice subsystems thermally equilibrate in $Cd_2Re_2O_7$, we performed time-resolved SHG measurements. The second-order electric-dipole susceptibility has been shown to couple linearly to the E_u structural order parameter below T_c [13,14]; therefore, the SHG intensity can be used as a sensitive measure of the lattice temperature. Figure 5(a) shows time-resolved SHG transients

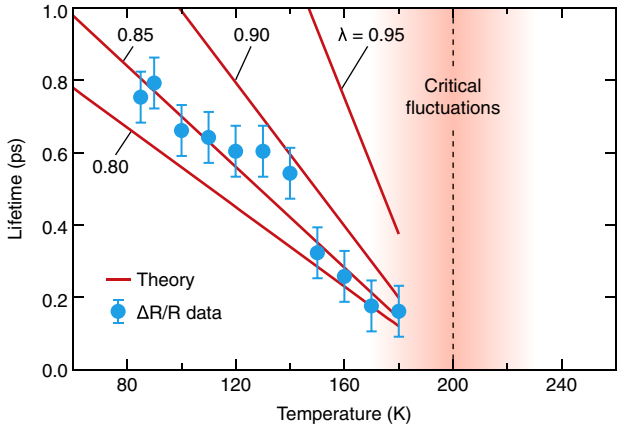

FIG. 4. Time-dependent Landau theory results. Calculated lifetime (τ) of oscillations of the structural order parameter away from its equilibrium value. Input parameters of the calculation include the observed mode frequency 2.5 THz and electronic damping rate 3.5 THz (denoted $\Omega_0/2\pi$ and $\gamma_0/2\pi$, respectively, in Ref. [22]), and different values of the reduced free-energy coupling constant $\lambda = g^2/bc$. The behavior $\tau \propto 1 - T/T_c$ observed by experiment is reproduced. For comparison, circles are experimental data from Fig. 3. The shaded region near T_c identifies where critical fluctuations are expected to be important and Landau theory no longer applies.

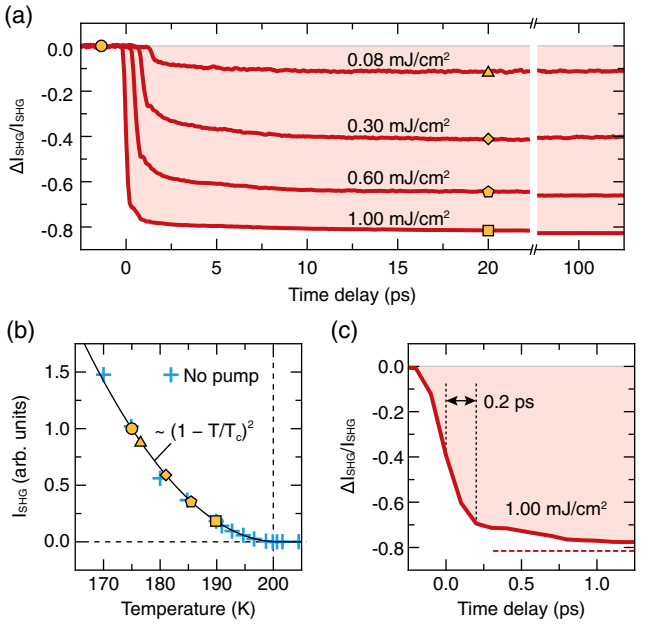

FIG. 5. Time-resolved second harmonic generation of $Cd_2Re_2O_7$. (a) Fractional change in SHG intensity $\Delta I_{SHG}/I_{SHG}$ at 175 K for a selection of pump fluences as a function of time delay after the pump pulse. Curves are horizontally offset for clarity. (b) SHG intensity as a function of temperature, demonstrating that $I_{SHG} \propto (1 - T/T_c)^2$. The orange symbols correspond to the intensity levels shown in (a) and illustrate the instantaneous temperature increase due to the pump pulse for different fluence values. (c) Close-up view of the reduction of I_{SHG} near time zero for a pump fluence of 1.00 mJ/cm^2. The majority of the intensity drop is complete by ~0.2 ps. The horizontal dashed line shows the quasisteady value at long times.

acquired at $T = 175$ K. For all pump fluences tested, we observe the SHG intensity drop to a lower value quickly upon pump excitation, indicating a rapid heating of the lattice, and then stay nearly constant at this value for over 100 ps. Since this far exceeds typical electron-lattice equilibration time scales, the equilibration must be complete once the intensity flattens. The long (> 100 ps) recovery time is likely due to slow heat diffusion away from the excited region, which is consistent with the reported low "amorphouslike" thermal conductivity of $Cd_2Re_2O_7$ [32]. To further verify that the system is equilibrated upon the flattening of intensity, we compared the actual temperature rise in this regime to the expected pump-induced temperature rise for an electron-lattice equilibrated system. The actual temperature rise can be obtained from the SHG intensity versus temperature curve measured from an unpumped sample [Fig. 5(b)], which exhibits a $I_{SHG} \propto (1 - T/T_c)^2$ scaling relation. For the data set in Fig. 5(a) acquired using a fluence of 1.00 mJ/cm^2, for example, the curve yields a temperature rise of $\Delta T \approx 15$ K at $t = 20$ ps. The expected temperature rise can be calculated using the equation $\Delta T \sim (1 - R)f/C_p\delta$, where R is the reflectivity, f is the fluence, C_p is the volumetric heat capacity, and δ is the optical penetration depth. Inputting $f = 1.00$ mJ/cm^2, $C_p \approx 2.3$ J/cm^3 K at $T = 175$ K [6,32,33], $R \approx 0.6$ and $\delta \approx 100$ nm at a pump wavelength of 1400 nm [34], we find $\Delta T \approx 17$ K, in good agreement with the actual measured temperature rise. This shows that the entirety of the pump pulse energy is accounted for by the increase in lattice temperature, which rules out the existence of a hotter electron subsystem since that would imply an incomplete transfer of energy to the lattice. Given that the equilibrated lattice temperature is nearly reached within a resolution limited time scale (< 0.2 ps) as shown in Fig. 5(c), the system can be well approximated as being in equilibrium over the time window that the coherent phonons are observed [Fig. 2(b)], which explains the efficacy of our time-dependent Landau theory. The rapid transfer of energy from the electronic to lattice subsystem is consistent with previous reports of strong electron-phonon coupling in $Cd_2Re_2O_7$ [7,35] and further supports our theory that the reciprocal process—a dissipation of the phonon energy into the electronic bath—is responsible for the observed phonon damping.

Although our analyses have focused on the electronically driven phase transition in $Cd_2Re_2O_7$, these results are generic to any system possessing a linear coupling between primary and secondary orders with different symmetries and may be an effective strategy to differentiate primary from secondary order parameters in a wide class of materials. For example, improper ferroelectrics [36,37] are driven by coupled primary structural order parameters,

and the ferroelectric mode of secondary nature in such systems should behave in much the same way as the E_u phonon mode in $Cd_2Re_2O_7$ observed here.

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*Author to whom correspondence should be addressed. dhsieh@caltech.edu

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