Persistence of magnetic order in a highly excited Cu^{2+} state in CuO

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We use ultrafast resonant x-ray diffraction to study the magnetic order in CuO under conditions of high electronic excitation. By measuring changes in the spectral shape of the Cu^{2+} magnetic $(1/2\ 0\ -1/2)$ reflection we investigate how an intense optical pump pulse perturbs the electronic and magnetic states. We observe an energy shift in the magnetic resonance at short times after the pump pulse. This shift is compared with expectations from band structure calculations at different electronic temperatures. This spectral line shift indicates that although the electrons are heated to effective electron temperatures far above T_N on a time scale faster than the experimental resolution, magnetic order persists in this highly excited state for several hundred femtoseconds.

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The dynamics of ordered magnetic systems on time scales approaching those of typical exchange interactions is of great interest both scientifically and for possible new data storage technologies. The discovery of subpicosecond demagnetization of metallic Ni by an intense femtosecond optical pulse has demonstrated that magnetism on fast time scales can lead to surprising new discoveries [1]. More recently, ultrafast magnetic domain switching using an ultrashort optical pulse has been demonstrated in intermetallic ferrimagnetic alloys [2]. This reversal can be understood as an ultrafast heating process where different magnetic sublattices of a ferrimagnet heat over different time scales [3]. This scenario leads to qualitatively new magnetic exchange interactions in the excited, transient state. In this context, it is of fundamental interest to understand how long a magnetically ordered system maintains its magnetic order after strong electronic excitation by an intense ultrafast optical laser pulse.

The ultrafast manipulation of spin systems has also been studied in antiferromagnetic (AFM) insulators [4]. In comparison to ferromagnetic and ferrimagnetic systems, much less is known about the time scales of the demagnetization of antiferromagnetic sublattices. Strong losses of magnetic order after optical excitation have been observed in manganites [5], nickelates [6], and cupric oxide (CuO) [7]. These experiments used the ultrafast x-ray pulses delivered by x-ray free electron laser sources to directly study the temporal response of the AFM order after excitation. A common result of all these studies is a very fast drop in the magnetic diffraction over a time faster than 400 fs. This suggests a strong suppression of the magnetic order on a time scale faster than that required for the electronic subsystem to equilibrate with the lattice. The experiments on CuO further showed that electronic

excitation can also lead at later times to a transition to another antiferromagnetic phase with a different magnetic ordering wave vector [7]. From these experiments it is clear that strong electronic excitation of antiferromagnetic materials can lead to significant changes in magnetic order. Little is known, however, about the chain of events connecting the initial optical excitation to these changes in magnetic order. Although we might expect that optical excitation in such systems can produce very high electronic temperatures of up to several thousand Kelvin on short time scales, it is not clear whether any level of magnetic order can persist under such conditions.

To address this issue, we investigate the magnetic dynamics of CuO under strong optical excitation using time-resolved resonant soft x-ray scattering. CuO orders magnetically below ~ 230 K [8–10] with an incommensurate cycloidal spin structure [11]. Below 213 K, the system transforms into a collinear antiferromagnet. Resonant soft x-ray scattering is particularly well suited to study the magnetic order of this material [12]. The resonance offers sensitivity to the magnetic moments and their electronic states. The electronic order in AFM CuO has been studied in detail with this technique [13,14]. The peculiar x-ray polarization dependence of the magnetic $(1/2\ 0\ -1/2)$ reflection has been attributed to orbital currents that couple directly to the spin moments.

To resolve the transient magnetic state of the system, we employ resonant magnetic x-ray scattering in a pump-probe scheme. An ultrashort laser pulse (800 nm, 40 fs) excites the CuO sample with a repetition rate of 60 Hz. The resonant x-ray scattering is then measured at a particular time relative to this excitation with 40 fs duration x-ray probe pulses from the Linac Coherent Light Source (LCLS) [15]. The diffractometer [16] installed at the soft x-ray materials science (SXR) station

FIG. 1. (Color online) Time dependence of the diffraction intensities from the magnetic $(1/2\ 0\ -1/2)$ reflection of CuO for various energies around the Cu L_3 edge normalized to unity for $t < t_0$. The data are taken at 200 K and with a pump fluence of 20 mJ/cm^2 . The shaded regions represent the data ranges used for the extraction of the spectral shape change. The lines are fits as explained in the text. Data for different energies are vertically shifted for better visibility.

measured the intensity of x-ray diffraction from the sample. The experimental setup and the sample growth conditions are described in Ref. [7]. Images of the magnetic $(1/2\ 0\ -1/2)$ reflection and the high temperature phase can be also found in this reference.

Figure 1 shows the time dependence of the magnetic $(1/2\ 0\ -1/2)$ reflection intensity acquired at various x-ray photon energies around the Cu L_3 edge in the commensurate magnetic low temperature phase (200 K) for an incident laser fluence of 20 mJ/cm^2 , just below the material damage threshold. At all measured energies we observe a sudden drop in intensity at a particular delay time. The magnitude of this initial intensity drop differs strongly for different energies, as does the subsequent behavior over the first few picoseconds after excitation. The difference in the recovery over the first picosecond is best seen when comparing the time dependence of the reflection taken at 927.6 and 928.7 eV. Whereas the intensity at 927.6 eV partially recovers after the initial drop, for 928.7 eV the intensity falls to an even lower level.

For a detailed comparison of time traces taken at different energies, the arrival time of the pump laser t_0 must be accurately estimated. For this purpose we perform a nonlinear least square fit to the experimental data using the functional

form

$$I(t, E) = \begin{cases} 1 & t < t_0 \\ 1 - A(E) \exp[-(t - t_0)/\tau] - B(E) & t > t_0 \end{cases}, \quad (1)$$

where $A(E)$ and $B(E)$ are fit parameters for each individual x-ray photon energy. The fit parameter τ represents the relaxation time and is assumed to be independent of the x-ray photon energy. In each step of the fitting routine this equation is evaluated and convolved with a Gaussian of 250 fs FWHM corresponding to the experimental time resolution. The changes in B represent the changes in the long-term drop of the diffraction intensity, whereas the changes in A represent the magnitude of short-term dynamics occurring over the relaxation time $\tau = 0.8\text{ ps}$, which is kept fixed in the individual fits. Although this phenomenological model describes the time traces reasonably, in the following discussion we do not attempt to interpret the values of these fit parameters, but instead use this procedure solely for the purpose of identifying data collected over particular ranges of delay times between the optical and x-ray pulses.

To better show the effect of the optical excitation, the energy dependence of the diffracted intensity of the sample before excitation is compared with the intensities after the excitation between 6 and 7 ps after t_0 . The spectral shape of the unperturbed magnetic reflection [Fig. 2(a)] exhibits

FIG. 2. (Color online) (a) Energy dependence of the undisturbed ($t < t_0$) magnetic $(1/2\ 0\ -1/2)$ reflection intensity in the vicinity of the Cu L_3 edge of CuO. (b) Energy dependence of the reflection intensities taken at 6–7 ps (averaged) after the 20 mJ/cm^2 laser pulse arrived. The line represents a model described in the text. The inset shows the undisturbed x-ray absorption spectrum for CuO.

a double peak structure as previously observed in static experiments [13]. The dip at 928.3 eV separating the two peaks is caused by strong self-absorption at the L_3 edge [inset Fig. 2(a)]. This energy also corresponds to the largest change in the normalized diffraction intensity immediately after laser excitation [Fig. 2(b)]. To understand the energy dependence of this laser-induced drop at t_0 around the absorption edge, we must account for the strongly energy-dependent changes in the x-ray penetration depth. This is important because the absorbed energy density from the pump laser is strongest near the surface and decays as the pump propagates into the bulk. This results in a strongly depth-dependent effect, where the changes induced by optical excitation decay strongly with distance from the surface of the sample. As the x-ray energy is tuned closer to resonance, the x-ray penetration depth gets smaller and probes mostly the region of strongly disturbed AFM order near the surface.

In order to model the effect of the pump excitation on the magnetic order, we must relate the absorbed energy density ρ to a local magnetic structure factor $S(\rho)$. As a first approximation, we can simply assume that an absorbed energy higher than a critical value ρ_0 will lead to a complete melting of the magnetic order and any excitation below this threshold has no effect on the unperturbed structure factor S_0 :

$$S(\rho) = S_0 \quad \text{for } \rho < \rho_0, \quad \text{and } 0 \quad \text{for } \rho > \rho_0. \quad (2)$$

Since ρ is a monotonically decreasing function of the depth z from the surface, there exists a depth d such that for $z < d$, $S = 0$, and for $z > d$, $S = S_0$. We can then estimate the intensity I diffracted from the sample normalized to the unperturbed intensity I_0 as

$$I(E)/I_0 = \int_d^\infty \exp[-\alpha(E)z] dz / \int_0^\infty \exp[-\alpha(E)z] dz, \quad (3)$$

where α is the x-ray-energy-dependent attenuation length in the sample, obtained by standard x-ray absorption spectroscopy (XAS) procedures [17,18]. To correct for the better energy resolution of the XAS data, we reduce the ratio between the absorption at resonance and off the resonance accordingly.

With this simple model, a molten CuO layer with thickness $d = 29$ nm describes qualitatively the energy dependence of the drop in magnetic diffraction intensities [see Fig. 2(b) as a solid line] caused by the laser excitation. The discrepancies between this model and the data may indicate that the assumption of a completely unperturbed structure factor for $z > d$ is incomplete, but the oversimplified nature of the single layer model makes a quantitative analysis of these discrepancies unreliable.

As an alternative approach, we instead compare the photon-energy-dependent changes in the diffraction intensity at different times after the initial excitation but before and after the subsequent relaxation at the time scale of 0.8 ps, which we observed in the fits to the phenomenological model. In this way we remove contributions from both completely molten and unexcited regions, as these are expected to change little within the first 2 ps. This leaves only the spectral changes due to electronic excitation. Specifically, we average the change in diffraction $I(\Delta t_1)$ collected between 0.25 and 0.75 ps and subtract this from the change $I(\Delta t_2)$ averaged between 1 and 2 ps (visu-

FIG. 3. (Color online) Energy-dependent difference in the normalized magnetic reflection intensities taken at early times after the 20 mJ/cm² laser pulse arrived ($\Delta t_1 = 0.25$ –0.75 ps and $\Delta t_2 = 1$ –2 ps) in the vicinity of the Cu L_3 edge of CuO. The line represents a model described in the text. The nominal sample temperature of 200 K is only 30 K below T_N . Inset: Energy-dependent difference of averaged absorption in the same time window excited with the same laser fluence.

alized by shaded areas in Fig. 1). Figure 3 shows the energy dependence of $(\Delta t_1 - \Delta t_2)/\Delta t_2$. The antisymmetric shape of this normalized difference in the energy dependence is strongly suggestive of a shift of the resonance to higher energies in the excited state. The energy-dependent difference of the x-ray absorption simultaneously collected in electron yield mode, does not show such a shift at early times (see inset Fig. 3). This indicates that the observed changes in the scattering resonance are not related to changes in the probe depth of the x rays. The observed difference spectrum can therefore be directly modeled by normalized differences between Lorentzians, since the Cu²⁺ ions have a single hole in the 3d shell ($3d^9$). A corresponding fit is shown in Fig. 3. This will significantly underestimate the spectral shift for a given nominal fluence as more strongly excited regions contribute less to the Bragg scattering signal. This results in a shift from the fit of 21 ± 9 meV.

To test whether this spectral line shift could indeed result from a highly excited antiferromagnetically ordered state in CuO, we have performed band structure calculations. These calculations were done both for a series of paramagnetic and for a series of AFM cells using the DMOL³ method [19,20] to calculate finite temperature Mermin density functional [21] energies for the electron system. The paramagnetic cells contained two CuO units, whereas the AFM cells contained eight CuO units. The calculation employed the Perdew-Burke-Ernzerhof [22] approximation for exchange and correlation. Brillouin zone integrations were performed on a k -point mesh of $12 \times 12 \times 8$ points for the paramagnetic and with $8 \times 12 \times 8$ for the AFM case.

To model the effect of the absorbed laser intensity, these calculations were performed as a function of electron temperature. These show that for increasing temperatures, the valence band and core level states shift in opposite

FIG. 4. (Color online) Calculated energy shifts of the Cu core $2p$ level, the Fermi energy, and the resulting total Cu $2p_{3/2}$ - $3d$ (transition energy).

directions (see Fig. 4), whereas the Fermi energy shifts initially to higher energies (red) and then lowers its energy before starting to increase rapidly. The core hole shifts continuously to lower energies (blue) due to the depopulation of the $3d$ states at elevated temperatures. These changes add up to an increase of the transition energy between the $2p_{3/2}$ and the Cu $3d$ valence states for increasing electronic temperature. An electronic temperature of approximately 2700 K is required to reproduce a 21 meV energy shift of the Cu $2p$ - $3d$ transition. The calculations show that the strong excitation modeled by elevated electronic temperature leads to a clear increase of the transition energy for the resonance in the excited state. It is important to realize that these states remain antiferromagnetically ordered. Excited states that no longer have an antiferromagnetic spin arrangement cannot contribute to the measured diffraction. This experimental evidence for the existence of highly excited magnetically ordered states is also supported by recent theoretical models that predict

highly excited antiferromagnetic states can be trapped in an ordered nonthermal state [23,24]. Interestingly, this trapping in the order of 0.5 ps might be related to the observed delay time of 400 fs observed for the incommensurate/commensurate magnetic phase transition when exciting CuO at $T = 207$ K.

Our measurement of the change in spectral shape of the $(1/2\ 0\ -1/2)$ magnetic reflection shows that although strong electronic excitation in the antiferromagnetic phase of CuO leads to a transient suppression of magnetic order, in some regions of the excited material antiferromagnetic order at very high electronic temperatures persists for a short time. The elevated electronic temperature is detected through a shift in the energy of the scattering resonance. A comparison of the data with band structure calculations suggests that effective electronic temperatures $T > 2000$ K would account for the observed shift of $E > 20$ meV. The persistence of magnetic order at these very high electronic temperatures (far above the Néel temperature) suggests that the spin subsystem remains to some extent isolated or trapped from the excitation on time scales of < 0.5 ps in CuO. This opens up a potentially interesting parameter space for ultrafast magnetism, where strongly elevated electronic temperatures are achievable without complete destruction of magnetism.

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