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Direct observation of Jahn-Teller critical dynamics at a charge-order Verwey transition

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By means of diffuse and inelastic x-ray scattering (DS,IXS), we probe directly the charge-ordering (CO) dynamics in the Verwey system $(\text{NaMn}_3)\text{Mn}_4\text{O}_{12}$, where a peculiar quadruple perovskite structure with no oxygen disorder stabilizes a nearly full $\text{Mn}^{3+}/\text{Mn}^{4+}$ static charge order at $T_{\text{CO}}=175$ K concomitant to a commensurate structural modulation with propagation vector $\mathbf{q}_{\text{CO}} = (\frac{1}{2}, \frac{1}{2}, 0)$. At T_{CO} , the IXS spectra unveil a softening of a 35.3 meV phonon at \mathbf{q}_{CO} . Lattice dynamical calculations enable us to attribute this soft phonon to a A_g mode whose polarization matches the Jahn-Teller-like distortion pattern of the structural modulation. This result demonstrates that the Jahn-Teller instability is the driving force of the CO Verwey transition in $(\text{NaMn}_3)\text{Mn}_4\text{O}_{12}$, thus elucidating a long-standing controversy regarding the mechanism of this transition observed in other mixed-valence systems like magnetite.

I. INTRODUCTION

The interplay of electron and lattice dynamics beyond the adiabatic approximation is at the forefront of research in the study of many-body systems, such as chemical reactions [1], ionization processes [2] and polaron transport [3]. Favorable conditions to investigate the non-adiabatic regime are usually found in mixed-valence systems, since charge fluctuations drive a strong electron-lattice coupling. One fascinating situation occurs when these fluctuations stabilize a static order of valence electrons. In a seminal paper [4], Verwey proposed that this situation is indeed realized as a static $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order (CO) in the archetypal mixed-valence system magnetite Fe_3O_4 , which would explain a pronounced structural distortion concomitant to a jump of the electrical resistivity at $T_V = 120$ K, known as Verwey transition. Verwey's picture has been subsequently questioned because a simple ionic description does not account for the complex structural changes occurring at T_V [5–11] and an alternative picture of polarons involving the dynamics of 3 Fe sites (trimerons) has been proposed [12, 13]. Subsequent studies of the critical dynamics at the transition have given evidence of electronic [14] but no phonon [13, 15] mode softening, which leaves open the question of the cooperative role of the electronic and lattice degrees of freedom on the transition.

A similar phenomenology is found in other mixed-valence systems like chemically doped manganites and nickelates with perovskite-like structure [16–18]. Also in these systems, a

static CO picture seems to be oversimplified due to disorder and electronic inhomogeneities inherent to chemically substituted compounds and alternative scenarios of dynamic charge fluctuations like Zener-polarons [19] have been proposed. In order to elucidate the above controversial points, here we investigate the Jahn-Teller (JT) dynamics governing the interplay of charge, orbital and spin orderings in mixed-valence transition-metal compounds, as discussed in the seminal papers by Goodenough [20] and by Wollan and Koehler [21] and extensively studied later [22–24]. The challenge is that a reliable investigation of this dynamics is hindered in most mixed-valence systems by the coexistence of charge-ordered and -disordered phases [24], incommensurate structural modulations like stripe phases [25] and electronic phase separation [26].

In the present work, we show that the above difficulty is overcome in the mixed-valence compound $(\text{NaMn}_3)\text{Mn}_4\text{O}_{12}$ (NaMnO) [27]. Similar to magnetite and manganites, at low temperatures, $T_{\text{CO}}=175$ K, NaMnO exhibits a $\text{Mn}^{3+}/\text{Mn}^{4+}$ CO transition of the Verwey type consisting of a cubic $Im\bar{3}$ to monoclinic $I2/m$ structural transition accompanied by a large jump of the electrical resistivity [28]. The unique characteristics of the quadruple perovskite structure $(AA'_3)B_4\text{O}_{12}$ allow to obtain an equal proportion of Mn^{3+} and Mn^{4+} ions in the octahedral B -sites without chemical substitutions. In addition, the peculiar four-fold coordination of the Mn^{3+} ions in the A' sites avoids the formation of oxygen defects. It turns out that $(\text{NaMn}_3)\text{Mn}_4\text{O}_{12}$ exhibits an almost full charge order of the B -site Mn^{3+} and Mn^{4+} ions concomitant to a zig-zag ordering of the $e_g 3d_{z^2}$ orbitals of the Mn^{3+} ions and leading to a comparatively simple structural modulation with commensurate propagation vector $\mathbf{q}_{\text{CO}} = (\frac{1}{2}, \frac{1}{2}, 0)$ [29].

The above favorable conditions prompt us to probe the lattice dynamics governing the CO Verwey transition in NaMnO .

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We first searched for structural anomalies at T_{CO} by diffuse x-ray scattering (DS), a suitable probe of static short-range structural correlations precursor of a structural transition. As reported on magnetite [30], these correlations produce anomalous DS intensities different from ordinary thermal diffuse scattering. Second, we investigated dynamic anomalies by inelastic x-ray scattering (IXS) at T_{CO} . Owing to the low- Z of Na, the scattered intensities mainly arise from the Mn and O atoms playing the dominant role in the lattice dynamics, a further favorable condition for both experiments.

II. EXPERIMENTAL DETAILS AND LATTICE DYNAMICAL CALCULATIONS

NaMnO single crystals were synthesized by high-pressure synthesis using a multi-anvil apparatus, as described elsewhere [31]. Prior to the DS and IXS experiments, two twinned single crystals selected from the same batch were mechanically made into the shape of a needle and etched down to 50 μm diameter with HCl in order to remove the damaged surface layer. The crystals were subsequently glued on a capillary and oriented with the [001] direction of the cubic lattice perpendicular to the scattering plane. For the DS measurements, the samples were submitted to shutterless exposure with wavelength $\lambda=0.715 \text{ \AA}$ at the ID28 beamline of the European Synchrotron Radiation Facility (ESRF). Scattered intensities were measured using a PILATUS 2M detector, as described elsewhere [32]. The rotation axis was set perpendicular to the beam and parallel to its polarization. The resolution was 0.1° per image and the exposure time was 0.6 s for each image. The data were analyzed using the CrysAlis software package and reconstructed using ESRF home-made software. Laue symmetry was applied to the data. The IXS experiment was performed at the ID28 beamline using a (999) Si monochromator line of wavelength $\lambda=0.6968 \text{ \AA}$, corresponding to an energy resolution of 3.0 meV. Constant- \mathbf{Q} energy scans were collected in transmission mode with $\mathbf{Q} \perp [001]$. For both experiments, the sample temperature was controlled using a liquid-nitrogen cryostream apparatus.

Lattice dynamical calculations for the cubic $Im\bar{3}$ phase of NaMnO were carried out using a shell model with pair-wise interionic interaction potential that includes short-range and long-range Coulomb terms. The parameters of the potential satisfy the conditions of static and dynamic equilibrium. The calculations, carried out using the current version of the DISPR software [33], include total energy calculations of the crystal structure, the phonon dispersion relation and the IXS cross section for each phonon mode. We computed the one-phonon IXS cross section for a given momentum \mathbf{Q} and energy ω transfer using the expression:

$$S(\mathbf{Q}, \omega) = A \sum_{\mathbf{q}, j} \frac{\hbar}{2\omega(\mathbf{q}, j)} \left\{ n[\omega(\mathbf{q}, j)] + \frac{1}{2} \pm \frac{1}{2} \right\} \cdot |F_j(\mathbf{Q})|^2 \delta(\mathbf{Q} - \mathbf{G} \mp \mathbf{q}) \delta[\omega \pm \omega(\mathbf{q}, j)] \quad (1)$$

where A is a proportionality constant and the sum is ex-

tended over all phonon modes of wave vector \mathbf{q} , energy ω and branch j , $n[\omega(\mathbf{q}, j)] = \left\{ \exp \left[\frac{\hbar\omega(\mathbf{q}, j)}{k_B T} \right] - 1 \right\}^{-1}$ is the Bose-Einstein distribution function for each mode, the sign \pm indicates anti-Stokes and Stokes processes, respectively, $\mathbf{G} = \mathbf{Q} \mp \mathbf{q}$ is a reciprocal lattice vector and $F_j(\mathbf{Q})$ is the dynamical structure factor:

$$F_j(\mathbf{Q}) = \sum_{k=1}^N f_k(\mathbf{Q}) \frac{\mathbf{Q} \cdot \mathbf{e}(\mathbf{q}, j, k)}{\sqrt{m_k}} e^{i\mathbf{G} \cdot \mathbf{R}_k} e^{-W_k(\mathbf{Q})} \quad (2)$$

where the sum is extended over all N atoms in the unit cell, f_k , m_k , $\mathbf{e}(\mathbf{q}, j, k)$, \mathbf{R}_k and W_k are the form factor, mass, normalized eigenvector, vector position and Debye-Waller factor of k -th atom and \mathbf{q} and j are the phonon wave vector and branch, as above.

III. DIFFUSE X-RAY SCATTERING RESULTS

By approaching gradually T_{CO} from room temperature, we expected to observe anomalous features in the DS data at the propagation vector \mathbf{q}_{CO} of the CO phase, which would reflect the incipient CO transition. Surprisingly, we instead found anomalous features at completely different wave vectors $\mathbf{Q} = (h \pm \frac{1}{3}, k \pm \frac{1}{3}, 0)$. As seen in Figs. 1, 2a-b and 3a-b, these features appear well above T_{CO} and become clearly visible already at $\approx 230 \text{ K}$; they consist of X- or bar-shaped clouds visible especially around the most intense $(4m, 0, 0)$ and $(2m + 1, 2n + 1, 0)$ peaks, respectively, and equivalent peaks of the cubic $Im\bar{3}$ phase (m, n integers). This observation is accompanied by a pronounced peak broadening along the [110] and $[1\bar{1}0]$ directions. The DS intensity profiles along these directions evolve continuously upon cooling down from room temperature. As seen in Fig. 3c, the tail of the Bragg peak is progressively enhanced until well-defined satellite peaks appear at $\mathbf{Q} = (h \pm \frac{1}{3}, k \pm \frac{1}{3}, 0)$ in the vicinity of T_{CO} . The second-order satellites at $\mathbf{Q} = (h \pm \frac{2}{3}, k \pm \frac{2}{3}, 0)$ are also visible. This result indicates an incipient structural modulation with propagation vector $\mathbf{q}_{DS} = (\frac{1}{3}, \frac{1}{3}, 0)$. Upon further cooling, the intensity of the DS anomalies progressively increases until they abruptly disappear at T_{CO} (see Fig. 1), concomitant to the appearance of the satellite peaks of the CO structural modulation at \mathbf{q}_{CO} . This indicates that the instability at \mathbf{q}_{DS} is suppressed by the CO instability at \mathbf{q}_{CO} .

IV. INELASTIC X-RAY SCATTERING RESULTS

In order to unveil the dynamics of this latent instability, we measured IXS spectra at $\mathbf{Q} = \mathbf{G}_{400} + \mathbf{q} = (4 \pm \xi, 0, 0)$ and $\mathbf{Q} = \mathbf{G}_{440} + \mathbf{q} = (4 \pm \xi, 4 \pm \xi, 0)$, *i.e.* along the [010] (Δ) and [110] (Σ) directions crossing the X- and bar-shaped DS anomalous features of Fig. 3a. We focused on the low-energy $\pm 30 \text{ meV}$ range, which enabled us to investigate the quasi-elastic (QE) peak and the longitudinal and mixed longitudinal-transverse acoustic phonons. Data were taken at 177 K, *i.e.*

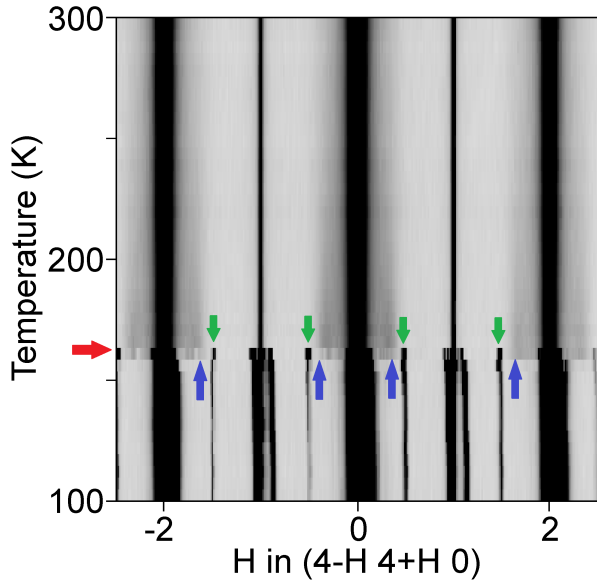


Figure 1. Temperature evolution of the DS intensity profile along the Σ direction crossing the (440) peak. Blue arrows indicate the position of the features at $\mathbf{q}_{\text{DS}} = (\frac{1}{3}, \frac{1}{3}, 0)$ that appear above 230 K and disappear upon cooling at the charge-ordering (CO) transition at $T_{\text{CO}}=175$ K, indicated by the red arrow. At T_{CO} , green vertical arrows mark the appearance of the superstructure reflections at $\mathbf{q}_{\text{CO}} = (\frac{1}{2}, \frac{1}{2}, 0)$. The noise in the data below T_{CO} is attributed to the formation of twin domains in the CO monoclinic structure.

just above T_{CO} , and at 207, 237 and 297 K. T_{CO} was precisely determined to be 175 K by cooling the sample until the satellite peaks of the CO phase appeared and by reducing the cooling rate until the thermal hysteresis disappeared. Representative spectra are shown in Fig. 4. The mode energies were determined by fitting the experimental phonon peaks using pseudo-Voigt functions. The Stokes and anti-Stokes lines of the acoustic phonons were fitted simultaneously by imposing the constraint set by the Bose factor for the intensities. Elastic lines were analyzed using a sum of Gaussian and Lorentzian line shapes to account for the contributions of the experimental resolution and of quasi-elastic scattering, respectively.

The main result is an enhanced intensity of the QE peak

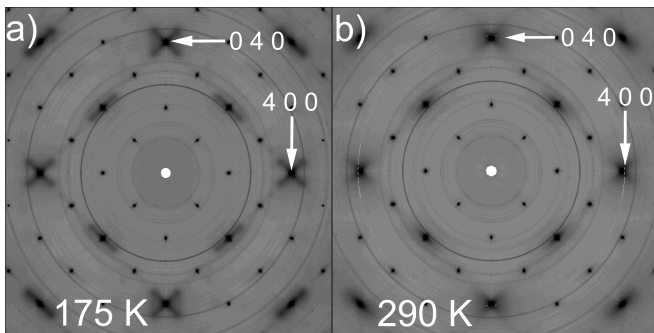


Figure 2. Detailed view of the reciprocal space maps of DS intensities near the (400) and (040) peaks at the CO transition temperature, $T_{\text{CO}}=175$ K (a), and at room temperature (b).

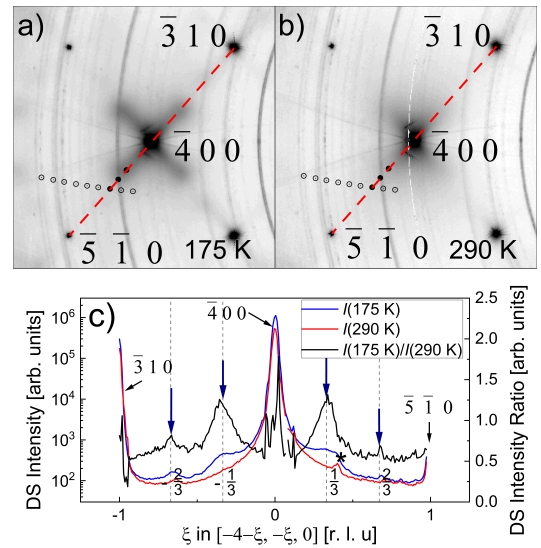


Figure 3. Color online. (a,b): reciprocal space DS intensity maps near the $(\bar{4}00)$ peak at $T_{\text{CO}}=175$ K and at room temperature (290 K). At T_{CO} , note the anomalous X-shaped features at $\mathbf{Q} = \mathbf{G}_{hk0} \pm \mathbf{q}_{\text{DS}} = (h \pm \frac{1}{3}, k \pm \frac{1}{3}, 0)$. Circles indicate the \mathbf{Q} points measured in the IXS experiment by using the main analyzer (full circles) and the extra analyzers (open circles) (see also text and Fig. 6). The broken red line indicates the direction of the intensity profiles shown in panel (c). (c): DS intensity profiles at $T_{\text{CO}}=175$ K and 290 K (red and blue lines) and ratio of these two profiles (black line) along the Σ direction crossing the $(\bar{4}00)$ peak, where the DS anomalous features are most visible. Blue arrows mark the wave vectors $(h \pm \frac{1}{3}, k \pm \frac{1}{3}, 0)$ and $(h \pm \frac{2}{3}, k \pm \frac{2}{3}, 0)$ where the anomalous DS intensities are observed. As in the DS data, quasi-elastic scattering is absent at room temperature. The asterisk indicates the polycrystal contribution to the diffraction pattern, visible as rings in panels (a,b).

upon cooling down to T_{CO} , similar to the case of incommensurate orbital ordering transition in the related compound $(\text{CaMn}_3)\text{Mn}_4\text{O}_{12}$ [34]. Interestingly, in the present case, the QE intensity progressively decreases by moving away from the above $(hk0)$ peaks, except for a sizable enhancement at $\mathbf{Q} = \mathbf{G}_{hk0} + \mathbf{q}_{\text{DS}}$ (see Fig. 4f), consistent with the behavior of the DS intensity profile of Fig. 3c. Upon cooling, no anomaly is seen in the mode dispersion at \mathbf{q}_{DS} (see Fig. 4e), which is again consistent with the DS result that the instability at \mathbf{q}_{DS} is suppressed at T_{CO} .

In the search for anomalous modes at the verge of the CO transition, in a second IXS experiment we measured the spectra along the same Δ and Σ directions as before in an extended energy range up to 90 meV, which enabled us to probe all modes. To look for anomalies, ideally one should follow the changes in the modes across T_{CO} . In practice, this is hindered by the formation of twinned domains in the monoclinic CO phase below T_{CO} . Still, the thermodynamic fluctuations of the CO order parameter near the transition can be sufficiently strong to produce measurable structural anomalies. It is expected that, slightly above T_{CO} , these fluctuations produce a measurable rounding in the temperature-dependence of the critical softening of the \mathbf{q}_{CO} phonon in the cubic phase.

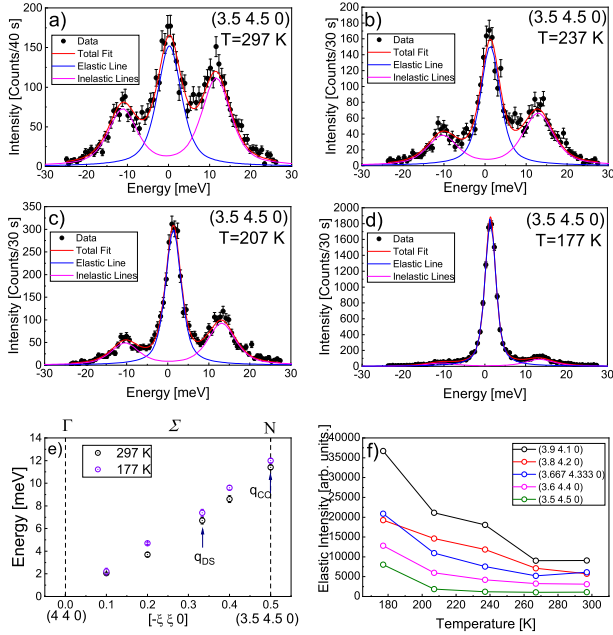


Figure 4. Color online. (a-d): Temperature evolution of the low-energy IXS spectra at $\mathbf{G}_{440} + \mathbf{q}_{\text{CO}} = (3.5, 4.5, 0)$ down to 177 K, i.e. just above T_{CO} . Note the increasing intensity of the elastic peak with decreasing T and the Stokes and anti-Stokes acoustic modes. Solid lines are a fit of these 3 peaks, as explained in text. (e): Dispersion of the acoustic mode along Σ at 297 and 177 K. Note a conventional mode hardening upon cooling, with no anomalies either at \mathbf{q}_{DS} or at \mathbf{q}_{CO} . (f): temperature dependence of the elastic intensity at various Q -points along Σ . The intensity increases upon cooling and decreases by moving away from \mathbf{G}_{440} , except at \mathbf{q}_{DS} , consistent with the X-shaped feature of the DS intensity in Fig. 3a.

This expectation is confirmed by the spectra taken along $[\bar{1}10]$ (Σ) (see Fig. 5). Upon cooling, note a pronounced 6% softening of an optical mode around 35 meV at the critical wave vector $\mathbf{Q}^* = \mathbf{G}_{\bar{4}00} - \mathbf{q}_{\text{CO}} = (-4.5, -0.5, 0)$. The critical behavior of the softening of this \mathbf{q}_{CO} phonon is evident by analyzing its dispersion along Σ . Additional \mathbf{Q} points collected by 8 extra analyzers located in the scattering plane or slightly above give further evidence of this softening. These additional points enable us to reconstruct the dispersion curve along an arc in the $(hk0)$ plane crossing $\mathbf{G}_{\bar{4}00}$, as indicated in Figs. 3a,b and 6a-c. In conclusion, Fig. 6 clearly shows a progressive mode softening as the critical wave vector \mathbf{Q}^* is approached while, away from \mathbf{Q}^* , the mode displays a conventional hardening upon lowering temperature. The magnitude of the softening is noteworthy, considering that it occurs in the fluctuation region of the cubic phase and that, in the absence of anomalies, a mode hardening should instead occur.

The \mathbf{Q} -dependence of the QE peak in Fig. 6b further indicates that the softening is correlated with incipient short-range structural correlations at T_{CO} . Knowing that this peak is well described by a Lorentzian function [35], we focus on the changes in the peak intensity and width observed at T_{CO} . The energy dependence of the peak carries significant information on the lattice dynamics because the peak is broader

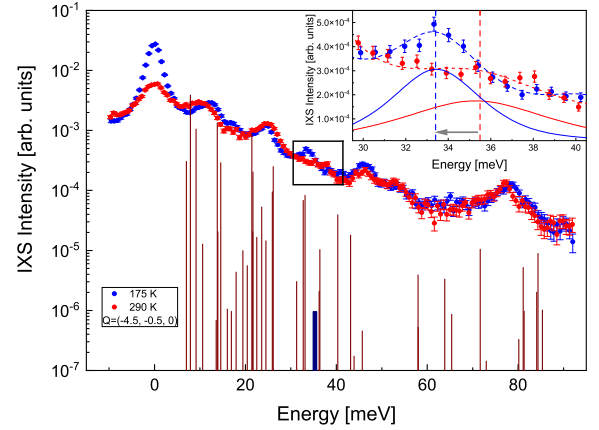


Figure 5. Color online. IXS spectra taken at 295 K (red points) and $T_{\text{CO}}=175$ K (blue points) at the CO wave vector $\mathbf{Q}^* = (-4.5, -0.5, 0)$. Vertical bars indicate the calculated energy and intensity of the A_g and B_u modes (see Table I). The A_g mode calculated at 35.3 meV, indicated by a thick blue bar, is attributed to the soft mode highlighted in the black frame and in the inset. The polarization of this A_g mode is given in Table II. Inset: detail of the softening region. Solid red and blue lines are a fit of the mode at 295 and 175 K, respectively. The vertical broken lines and the arrow indicate the ≈ 2 meV energy shift of the mode. Broken lines are a fit of the two spectra including the contribution of all modes.

than the instrumental resolution. We exclude that the broadening is due to the contribution of low-energy acoustic phonons, for these phonons are located at higher energies. Our analysis of the peak data as a function of \mathbf{Q} shows a significant peak broadening at \mathbf{Q}^* (see Fig. 6b), which corroborates the picture of critical behavior of the lattice dynamics at \mathbf{q}_{CO} .

V. PHONON CALCULATIONS RESULTS

We should now try to single out the driving force of the lattice softening by identifying the symmetry of the soft phonon. In the high-temperature cubic $Im\bar{3}$ phase, the small point group is cubic T_h at Γ and monoclinic C_{2h} at $\mathbf{q}_{\text{CO}} = \mathbf{N}$, where the softening is observed, so the symmetry of the measured phonons at \mathbf{q}_{CO} is either A_g or B_u . In NaMnO, there are 8 modes of the former symmetry and 26 of the latter. We then carried out lattice dynamical calculations on the high-temperature cubic $Im\bar{3}$ phase. The room temperature structural data used as input for the calculations are taken from [27]. In Table I below we report the calculated energies and intensities of the 34 A_g or B_u modes, symmetric with respect to σ_z , at the wave vector \mathbf{Q}^* measured in the IXS experiment. We do not consider the remaining 26 B_g or A_u modes, for they are antisymmetric with respect to σ_z and therefore not measured in the present IXS geometry. In Table II, we give the eigenvector of the relevant A_g mode of calculated energy 35.3 meV, attributed to the soft mode observed by IXS.

The reliability of the calculations is seen in Fig. 7, where one notes the agreement between experimental and calculated

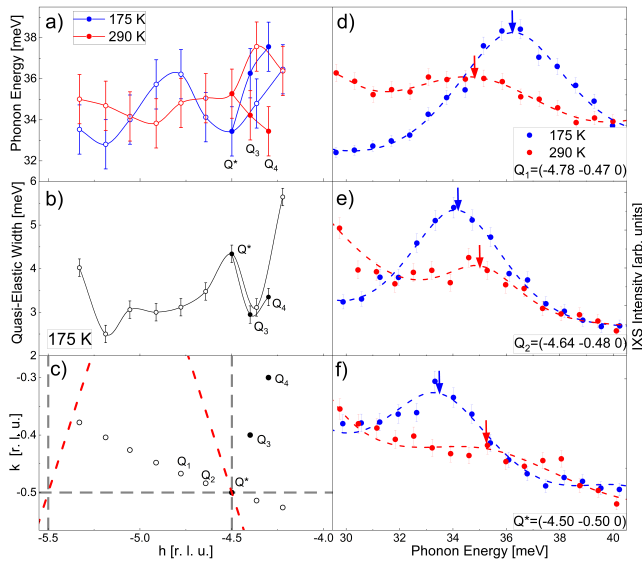


Figure 6. Color online. (a): IXS dispersion of the soft mode of Fig. 5 taken at 290 K and $T_{CO}=175$ K along the $[\bar{1}10]$ (Σ) direction and along the arc indicated in panel (c). Full and open symbols are points measured by the main and extra analyzers, respectively (see text). Lines are a guide to the eye. Note a pronounced softening at T_{CO} by approaching the wave vector $\mathbf{Q}^* = \mathbf{G}_{400} - \mathbf{q}_{CO}$. (b): \mathbf{Q} -dependence of the width of the quasi-elastic peak at T_{CO} . Note the peak broadening at \mathbf{Q}^* . Full and open symbols are as in (a) and (c). (c): Location in the $(hk0)$ plane of all measured \mathbf{Q} -points in reciprocal lattice units [r.l.u.]. Broken red and gray lines indicate the Brillouin zone boundary of the cubic unit cell and of the monoclinic supercell, respectively. (d-f): detail of the spectra at $\mathbf{Q}^* = (-4.5, -0.5, 0)$, $\mathbf{Q}_2 = (-4.64, -0.48, 0)$ and $\mathbf{Q}_1 = (-4.78, -0.47, 0)$. Broken lines are a fit of the full spectrum to which all modes contribute. Arrows indicate peak position.

dispersions along the representative $[\bar{1}10]$ direction within the experimental resolution. Hereafter, we focus on the above 34 A_g and B_u modes at the \mathbf{Q}^* wave vector of interest. In Fig. 5, we note the agreement between experimental and calculated positions and intensities of these modes at \mathbf{Q}^* (see Table I for a full list of the calculated values). Thus, we are confident that the shell model employed in the calculations is reliable to identify the polarization of the soft mode.

Within the energy resolution of the IXS experiment, $\Delta E=3.0$ meV, three of the calculated modes, two with B_u symmetry and one with A_g symmetry, have energies of 35 ± 1.5 meV at \mathbf{Q}^* (see Table I). However, only the polarization of the A_g mode, of calculated energy 35.3 meV, matches the displacement of the Mn and O atoms governing the structural modulation in the CO phase previously reported [29]. This is understood using the straightforward symmetry argument that A_g is the totally symmetric representation of the C_{2h} small group of the modulated structure. The match between distortion pattern of the phonon and structural modulation is evident in Fig. 8. Note, in particular, the JT-like elongation of half of the MnO_6 octahedra in the pristine cubic cell along the apical $[100]$ or $[010]$ direction, leading to a zig-zag pattern along the $[110]$ direction of the \mathbf{q}_{CO} propagation vector. This leads to

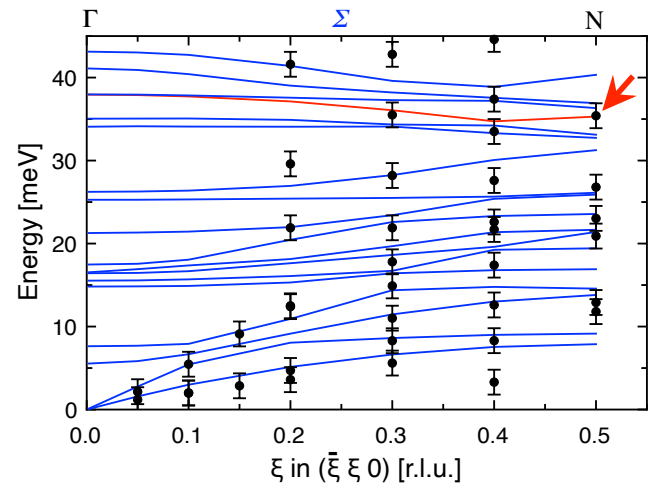


Figure 7. Experimental (points) and calculated (lines) phonon dispersion along the $[\bar{1}10]$ (Σ) direction in reciprocal lattice units [r.l.u.]. The experimental points have been measured by IXS at 290 K (see main text). The red line indicates the mode attributed to the soft mode observed experimentally at the zone boundary $N = (-\frac{1}{2}, \frac{1}{2}, 0) = \mathbf{q}_{CO}$ marked by a red arrow. At this point the mode symmetry is A_g . See in Table I the list of calculated mode energies and intensities at N and in Table II the calculated polarization of the soft A_g mode.

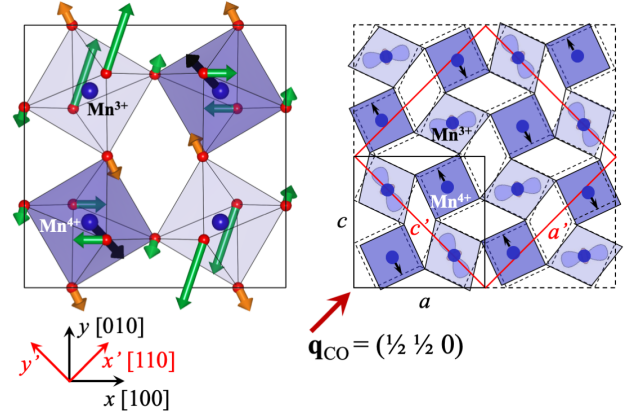


Figure 8. Color online. Left: calculated polarization of the A_g 35.3 meV mode at $\mathbf{q}_{CO} = (\frac{1}{2}, \frac{1}{2}, 0)$ in the parent cubic $Im\bar{3}$ symmetry, attributed to the soft phonon observed by IXS. Arrows indicate the displacements (in scale) of the octahedral B -site Mn and O atoms. The values of the displacements are reported in Table II for all atoms. Dark and light blue colors denote the two distinct $4e$ and $4f$ B-sites in the A_g symmetry (see Table II). Right: Schematic structural modulation described by the propagation vector \mathbf{q}_{CO} in the monoclinic $C2/m$ symmetry, concomitant to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering at T_{CO} (adapted from [29]). The unit cell of the parent $Im\bar{3}$ structure and the supercell are indicated by thick solid black and red lines, respectively. Thin broken and solid black lines represent the B -site MnO_6 octahedra in the parent and distorted structures, respectively. Note the match between the pattern of the atomic displacements of the A_g mode and the structural modulation, in particular the zig-zag displacement of the Mn^{4+} ions (black arrows) and the Jahn-Teller elongation of the octahedra of the Mn^{3+} ions (orange arrows) leading to a zig-zag orientation of the $3d_{z^2}$ orbitals of these ions.

the formation of the $\sqrt{2} \times \sqrt{2}$ supercell previously reported in the monoclinic CO phase [29]. The observed JT distortion of these octahedra is as expected for the JT-active Mn^{3+} ions, consistent with the scenario of $\text{Mn}^{3+}/\text{Mn}^{4+}$ order previously reported. The remaining octahedra, occupied by the Mn^{4+} ions in the CO phase, exhibit a modest distortion with negligible volume change, for these ions are not JT active. They instead exhibit an alternated displacement along the [110] direction to accommodate the elongation of the Mn^{3+} octahedra. In summary, the CO modulated structure arises from a critical slowing down of the Jahn-Teller 35.3 meV A_g phonon.

VI. CONCLUSIONS

In conclusion, we directly observed the critical lattice dynamics at the CO Verwey transition in the mixed-valence compound NaMnO by means of DS and IXS. This critical dynamics consists of a phonon softening at the propagation vector \mathbf{q}_{CO} of the CO modulated structure. Remarkably, the softening is sizable already in the thermodynamic fluctuation region of the cubic phase slightly above T_{CO} . Lattice dynamical calculations enabled us to attribute the softening to a A_g optical mode coupled to the JT dynamics of the MnO_6 octahedra in presence of an incipient $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge disproportionation. The match between calculated polarization of the soft phonon and experimental distortion pattern of the CO phase

shows that the JT instability is the microscopic mechanism of the transition. The data also unveil a competing structural instability with a distinct commensurate propagation vector appearing at temperatures much higher than T_{CO} and suppressed by the CO instability. Further studies using experimental probes of the short-range crystal structure, such as extended X-ray absorption fine-structure (EXAFS), may further elucidate the long-standing controversy on the scenarios of static charge ordering vs. dynamical charge fluctuations governing the physics of mixed-valence transition-metal oxides including magnetite, manganites and superconducting cuprates.

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VII. APPENDIX

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Table I. Calculated energy and intensity of the 34 A_g or B_u phonon modes measured in the IXS experiment at the critical wave vector $\mathbf{q}_{\text{CO}} = (\frac{1}{2} \frac{1}{2} 0)$ of the charge-order Verwey transition. The calculated energy and intensity values are plotted graphically as vertical bars in Figure 5. In bold the A_g mode attributed to the soft mode observed in the IXS experiment (see Figures 5 and 6).

Energy [meV]	Calculated intensity [arb. units]	Symmetry
7.9	3.89×10^{-3}	A_g
9.2	1.05×10^{-3}	B_u
13.8	1.32×10^{-3}	B_u
14.6	2.90×10^{-4}	A_g
16.9	9.67×10^{-7}	A_g
19.4	9.90×10^{-6}	B_u
21.4	8.75×10^{-4}	A_g
21.7	2.01×10^{-4}	B_u
23.6	5.30×10^{-5}	A_g
25.9	9.47×10^{-5}	B_u
26.1	2.51×10^{-4}	A_g
31.3	3.02×10^{-6}	B_u
31.6	0.00	A_g
32.7	6.80×10^{-5}	B_u
33.1	8.30×10^{-5}	B_u
35.3	9.59×10^{-7}	A_g
36.3	1.03×10^{-5}	B_u
36.9	0.00	A_g
40.4	3.93×10^{-5}	B_u
42.2	0.00	A_g
43.1	1.80×10^{-5}	A_g
45.7	4.56×10^{-7}	B_u
57.9	3.89×10^{-6}	B_u
58.0	5.22×10^{-7}	A_g
63.9	3.33×10^{-6}	B_u
65.4	8.63×10^{-7}	A_g
71.7	1.05×10^{-5}	B_u
72.9	1.43×10^{-7}	A_g
80.2	3.31×10^{-7}	B_u
81.1	5.19×10^{-6}	A_g
82.9	8.25×10^{-9}	A_g
84.1	2.02×10^{-6}	B_u
84.4	8.89×10^{-6}	A_g
85.3	1.01×10^{-6}	B_u

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Table II. Calculated atomic displacements, u_x , u_y and u_z , along the x -, y -, and z -directions for the 35.3 meV A_g phonon. Atomic site label, Wyckoff position and symmetry are given for both parent $Im\bar{3}$ and distorted $C/2m$ structures. Atomic coordinates are given in reduced lattice units. The structural data of the $Im\bar{3}$ structure are taken from [27], with unit cell parameter $a = 7.3036 \text{ \AA}$. The atomic coordinates of the $C/2m$ structure are given by choosing a unit cell with unique axis z and origin at the centre, corresponding to the $I112/m$ space group [36].

Atomic site			Atomic coordinates			Atomic displacements [arb. units]					
Parent $Im\bar{3}$ structure			Distorted $C/2m$ structure			x	y	z	u_x	u_y	u_z
Na	$2a$	$m\bar{3}$	Na	$2a$	$2/m$	0	0	0	0	0	0
			MnA'1	$2b$	$2/m$	0	0	1/2	0	0	0
MnA'	$6b$	mmm	MnA'2	$2c$	$2/m$	1/2	0	0	-0.53	0.39	0
			MnA'3	$2d$	$2/m$	0	1/2	0	-0.03	0.65	0
MnB	$8c$	$\bar{3}$	MnB1	$4e$	$\bar{1}$	1/4	1/4	1/4	0.32	-0.34	-0.19
			MnB2	$4f$	$\bar{1}$	1/4	1/4	3/4	0	0	0
			O1	$4i$	m	0.3132	0.1828	0	0.31	0	0
			O2	$4i$	m	0.6868	0.1828	0	0.22	0.65	0
O	$24g$	m	O3	$8j$	1	0.1828	0	0.3132	0.11	-0.21	0.06
			O4	$8j$	1	0	0.3132	0.1828	-0.05	-0.19	-0.09