Origin of low-energy excitations in charge-ordered manganites

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Abstract – The low-energy excitations in the charge-ordered phase of polycrystalline La0.25Ca0.75MnO3 are explored by frequency-domain terahertz spectroscopy. In the frequency range from 4 cm−1 to 700 cm−1 (energies from 0.4 meV to 90 meV) and at temperatures down to 5 K, we do not detect any feature that can be associated with the collective response of the spatially modulated charge continuum. In the antiferromagnetically ordered phase, broad absorption bands appear in the conductivity and permittivity spectra around 30 cm−1 and 100 cm−1 which are assigned to former acoustic phonons optically activated due to a fourfold superstructure in the crystal lattice. Our results indicate that characteristic energies of collective excitations of the charge-ordered phase in La0.25Ca0.75MnO3, if any, lie below 1 meV. At our lowest frequencies of only few wavenumbers a strong relaxation is observed above 100 K connected to the formation of the charge-ordered state.

Introduction. – Manganese oxides R1−xAzMnO3 (with R being rare earth and A alkaline elements) represent a unique playground for investigating electronic correlation effects in solids because the competing interactions related to charge, spin, orbital and lattice degrees of freedom are of comparable strength, resulting in a rich phase diagram [1–3]. In recent years much effort has been devoted to the intriguing phenomenon of charge ordering (CO), which for La1−xCa2MnO3 in the concentrations range 0.5 ⩽ x ⩽ 0.85 takes place at rather high temperatures. Below TCO the system changes also its magnetic properties from a paramagnetic to an antiferromagnetic (AFM) state. It was suggested that the mixed-valence manganese ions dissociate into two subsystems with integer valences, Mn3+ and Mn4+ which occupy different atomic sites of the lattice, causing spatial stripes of commensurate doping with a period being a multiple of the lattice constant in the a direction [4–6].

Later it was found, however, that the charge modulation does not have full amplitude and that the wave vector q = a∗(1 − x) is concentration dependent (a∗ is the reciprocal lattice vector) and not necessarily tied only to atomic sites [7–10].

Recently, it was suggested [11] that the ordering in manganites can be of Fröhlich-Peierls type leading to a charge density wave (CDW) [12]. Several observations seem to support this idea. Fermi-surface nesting [13] was observed, together with transport signatures of a CDW, such as nonlinear dc resistivity and broad-band noise [14,15]. Terahertz and infrared (IR) spectroscopic measurements on Nd1−xSr2MnO3, La1−xCa2MnO3 and Pr1−xCa2MnO3 have revealed resonances in the far-infrared range which are interpreted by the authors as collective modes arising from the CDW condensate [16,17]. Although the idea seems intriguing [18] and applicable to other charge-ordered systems such as cuprates [19–22] or organics [23], more experiments are needed to verify a CDW state in charge-ordered manganites [24,25]. Here we present investigations of the

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low-energy electrodynamics of La$_{0.25}$Ca$_{0.75}$MnO$_3$ which clearly identify the low-frequency excitations simply as former acoustic phonons optically activated by folding of the Brillouin zone caused by a superstructure in the crystal lattice.

**Experimental.** – Polycrystalline samples of La$_{0.25}$Ca$_{0.75}$MnO$_3$ were prepared by sol-gel method as described in ref. [26] where the grain size can be selected by annealing at different temperatures. The average particle diameter was determined by field-emission scanning microscopy and X-ray using Scherrer formula; the structure of the samples was characterized by X-ray diffraction. For the optical measurements, we prepared pellets of 10 mm diameter and thickness varying from approximately 0.1 to 0.6 mm. Optical studies were performed in the THz range using a coherent-source spectrometer in a Mach-Zehnder arrangement [27] that allows us to directly measure the complex conductivity \( \sigma(\nu) \) or complex permittivity \( \varepsilon(\nu) \) at frequencies from \( \nu = 1 \) up to 50 cm$^{-1}$, in the temperature interval from 2 to 300 K and in magnetic field up to 8 T. The same pellets of La$_{0.25}$Ca$_{0.75}$MnO$_3$ also the far-infrared reflectivity was measured up to 700 cm$^{-1}$ using a Fourier transform infrared spectrometer in order to obtain the real parts of the conductivity \( \sigma(\nu) \) and permittivity \( \varepsilon(\nu) \) in a wide frequency interval from 4 up to 700 cm$^{-1}$.

**Results.** – In fig. 1a the conductivity spectra of La$_{0.25}$Ca$_{0.75}$MnO$_3$ pellets with grains of 1 \( \mu \)m size are plotted for different temperatures. Above the charge-ordering temperature \( T_{CO} \approx 240 \) K the conductivity is metal-like, it is almost frequency independent below 30 cm$^{-1}$, and gradually decreases for higher frequencies. Beyond 200 cm$^{-1}$ phonon features become dominant because incompletely screened by itinerant carriers.

When the sample is cooled below \( T_{CO} \), the conductivity spectra change their character qualitatively, from metallic to dielectric. The values of \( \sigma(\nu) \) drop drastically, especially at the lowest frequencies of few wave numbers. The permittivity \( \varepsilon(\nu) \) decreases for lower values (at \( T = 300 \) K) up to large positive values; the slope \( d\sigma/d\nu \) becomes negative (cf. fig. 3a). As demonstrated in the inset of fig. 1a, in the range \( T_N \approx 140 \) K < \( T < T_{CO} \approx 240 \) K the conductivity is thermally activated \( \sigma(T) \propto \exp\left(-E_{act}/k_BT\right) \) with \( E_{act}=0.13 \) eV, indicating an energy gap \( 2\Delta = E_{act} \) (pseudogap for \( T > T_{CO} \)) in the density of states. It is generally accepted that this gap or pseudogap is caused by the long-range charge order below \( T_{CO} \) or by correspondent order-parameter fluctuations above \( T_{CO} \) [28].

In the AFM phase (\( T < T_N \)), an absorption band appears in the range 20 to 40 cm$^{-1}$ getting more pronounced as the temperature is lowered. A close inspection of this band reveals two resonances located at frequencies 25 ± 3 and 38 ± 3 cm$^{-1}$, which are basically temperature independent. When we reduce the grain size from 1000 to 40 nm, the band gradually disappears, as is demonstrated by fig. 1b. In addition, a less intense and broader absorption band can be identified in the range 60–100 cm$^{-1}$. It is also more pronounced in the AFM phase, and loses intensity in samples with smaller grains. At our lowest frequencies of only few wave numbers a strong relaxation is observed above 100 K which vanishes as the temperature decreases \( T \to 0 \).

**Discussion.** – It is generally accepted that the simple picture based on ordering of Mn$^{3+}$–Mn$^{4+}$ ions is too rough to account for all peculiarities of manganites. To explain the CO state with charge modulation of non-integer amplitude and (in general) incommensurate wave vector \( \mathbf{q} = \mathbf{a}^*(1-x) \), a CDW ground state was proposed [14,15,24].
Kida et al. [16] assigned a low-frequency (16–24 cm$^{-1}$) absorption peak observed in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ to a collective excitation (phason) of the CDW state. Along these lines, Nucara et al. [17] attributed the asymmetric bands, they recently detected between 15 and 60 cm$^{-1}$ in a series of manganites including La$_{0.25}$Ca$_{0.75}$MnO$_3$, to a combination of CDW phason and amplitudon responses, and another peak below 10 cm$^{-1}$ to a pinned CDW-phason.

In contrast to these suggestions and based on our comprehensive spectroscopic investigations of the low-frequency excitations in La$_{0.25}$Ca$_{0.75}$MnO$_3$ we show that there are no spectroscopic features at frequencies down to 4 cm$^{-1}$ which could correspond to a collective response of the CO-condensate. We assign the resonance absorptions between 20 and 40 cm$^{-1}$ and around 100 cm$^{-1}$ to acoustic phonons that become optically active after the folding of the Brillouin zone due to evolution of a superstructure in the crystal lattice accompanying the charge and antiferromagnetic orderings. Indeed, X-ray studies of La$_{0.25}$Ca$_{0.75}$MnO$_3$ evidence that the orthorhombic unit cell quadruples along the $a$-axis when cooled below T$_{CO}$ [29], meaning that the high-temperature space group Pnma is transformed to P2$_1$/m. Consequently, the CO transition has to be described by an order parameter that is transformed according to the $\Sigma_1$($q_x = a^*/4$) irreducible representation of the space group Pnma. As a result of the Pnma ↔ P2$_1$/m structural phase transition, the phonons with the wave vector $q_x = a^*/4$ and $q_x = a^*/2$ are folded to the Brillouin zone center (Γ-point) of the monoclinic P2$_1$/m phase. They are split into two types of phonons – symmetric (gerade) and antisymmetric (ungerade), relative to the center of inversion; in other words, they are split into the ($g$, $u$) pairs. The gerade modes ($A_g$ and $B_g$) become optically Raman-active phonons, while the ungerade modes ($A_u$ and $B_u$) form polarization waves and become IR-active. In the case of La$_{0.25}$Ca$_{0.75}$MnO$_3$ the infrared activity of the corresponding modes is promoted by a dipole moment produced by spatial charge disproportionation which has to include all ions of the new unit cell together with the valence difference on manganese ions.

Analysis of the spectra shows that the oscillator strength of the IR folding modes is much smaller than the strength of the IR phonons. For instance, at $T = 5$ K the oscillator strength of the band at 20–40 cm$^{-1}$ equals $\Delta \nu F^2 \approx 1.4 \times 10^4$ cm$^{-2}$ while that of main IR phonons is about 1 to 3 $\times 10^5$ cm$^{-2}$. This provides another indication of the smallness of the charge transfer between the manganese ions and of the lattice distortion (seen also in the relative intensity of the 4a superlattice Bragg peaks [29]); both factors contribute to the strength of the folded bands. In general, during structural phase transitions the new lattice modes of the lower-symmetry phase can have larger or smaller intensity depending on the amplitude of the distortion, as known from infrared spectra of ferroelectrics, for instance [30,31].

The described transformation of phonon branches is qualitatively depicted in fig. 2, in close resemblance with calculations of the phonon frequencies of undoped LaMnO$_3$ [32]. It now becomes obvious that the absorption band observed in La$_{0.25}$Ca$_{0.75}$MnO$_3$ at 20–40 cm$^{-1}$
corresponds to the modes with the wave vector $\mathbf{q} = a^*/4$, while the broad set of superimposed bands at frequencies around 100 cm$^{-1}$ is associated with the Brillouin-zone-boundary modes of wave vectors $\mathbf{q} = a^*/4$. Significant broadening of the phonon modes can be connected to the polycrystalline nature of the samples with all three crystallographic directions contributing to the optical response and with phases of other symmetries present below $T_N$, like a phase with the 3a superlattice [29]. The appearance of the broad band at 20–40 cm$^{-1}$ only in the AFM phase and not right below $T_{CO}$ agrees well with the temperature evolution of the weight fraction of the new 4a phase which starts to increase below $T_{CO}$ but reaches its full strength only below $T_N$. Note that the magnetic origin of the band can definitely be ruled out because the AFM resonance modes are weaker by more than a factor of 100 and their resonance frequencies are strongly temperature dependent [33].

As seen from fig. 1b, the phonon bands weaken gradually in samples with smaller grain size, indicating a suppression of the 4a-superlattice in small nano-crystallites. Reduction of grain sizes causes an intensity decrease, but not a full suppression of the CO gap $2\Delta$ and correlation strength $2\Delta/T_{CO}$ (inset in fig. 1b), in accordance with magnetic [34] and optical measurements [28], indicating weak coupling of charge and magnetic order parameters to the lattice. It would be of interest to investigate the low-frequency response and nano-size effects in manganites with other alkali-metal concentrations since $x$ determines the stability of and the balance between the different interactions and also the frequency position of the folded phonon modes, according to the wave vector of the lattice modulation $\mathbf{q} = a^*(1-x)$ [8,9,35].

In fig. 3 we present the pronounced relaxational behavior of the real and imaginary parts of the dielectric permittivity, $\varepsilon' (\nu)$ observed at our lowest frequencies. The relaxation becomes weaker as the temperature is lowered and the dc conductivity decreases, indicating a close connection to the itinerant charge carriers. The characteristic frequency $1/(2\pi\tau_D)$ (with $\tau_D$ the relaxation time), at which the maximum of $\varepsilon'' (\nu)$ is seen in a simple Debye case [36] has to be located well below our frequency range ($\nu < 4$ cm$^{-1}$). This value is too low for the relaxation to be explained by trivial geometrical localization within the grains: from the metallic strands model the relaxation is expected at 300 cm$^{-1}$ and higher [37]. We thus expect that the observed relaxational dispersion in La$_{0.25}$Ca$_{0.75}$MnO$_3$ is intrinsic and linked to the CO process, that might be similar to the “order-disorder” phase transitions, for instance, in ferroelectrics or dipole glasses (relaxors). The dynamics of such systems is commonly described by a relaxational behavior of a certain response function, with a single relaxation time or distribution of those, revealing definite temperature dependences [38]. Alternatively, Efremov et al. suggested that in manganites the interplay between charge and magnetism can lead to ferroelectricity with the dipole moments aligned along the diagonal between the $a$ and $b$ axes [39]. The transition to such a ferroelectric phase could also be responsible for the dielectric relaxation observed in La$_{0.25}$Ca$_{0.75}$MnO$_3$.

**Conclusion.** – We have investigated the conductivity and dielectric permittivity of polycrystalline La$_{0.25}$Ca$_{0.75}$MnO$_3$ in the frequency range from 4 to 700 cm$^{-1}$ (quantum energies 4 to 90 meV) using coherent-source THz spectroscopy, combined with FTIR measurements. In the antiferromagnetically ordered phase at $T < T_N \approx 140$ K, resonance-like absorption bands appear in the spectra at 20–40 cm$^{-1}$ and around 100 cm$^{-1}$. We show that the bands are not connected to the collective response of the charge-ordered subsystem but are acoustic phonons which gain optical activity when folded to the Brillouin zone center due to a structural phase transition resulting in a fourfold superlattice along the $a$-direction. With decreasing size of the crystallites, the 4a-superlattice and hence the absorption bands are gradually suppressed while the charge and antiferromagnetic orders survive, indicating a weak coupling of the correspondent order parameters to the lattice. Our results evidence that all optically active excitations of the electronically correlated phase in La$_{0.25}$Ca$_{0.75}$MnO$_3$ manganite, if any, should have energies smaller than 0.4 meV. Regardless of their microscopic origin, charge-modulated systems that have correlations of the order of 0.1 to 1 eV (as characterized by the charge gap) in general exhibit rather soft excitations observed at microwave-, radio-, and audio-frequencies [12,22,40]. At the lowest frequencies 4–20 cm$^{-1}$ a strong relaxation is observed above 100 K in all samples. It may indicate
an order-disorder character of the charge-order phase transition in La$_{0.25}$Ca$_{0.75}$MnO$_3$.

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