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(Received 23 April 2009; published 13 August 2009)

We demonstrate that the onset of complex spin orders in ACr$_2$O$_4$ spinels with magnetic and Jahn-Teller active A = Fe and Cu ions lowers the lattice symmetry. This is clearly indicated by the emergence of anisotropic lattice dynamics—i.e., by the pronounced phonon splittings—even when experiments probing static distortions fail. The crystal symmetry in the magnetic phase is reduced from tetragonal to orthorhombic for both compounds. The conical spin ordering in FeCr$_2$O$_4$ is also manifested in the hardening of the phonon frequencies. In contrast, the multiferroic CoCr$_2$O$_4$ with no orbital degrees of freedom shows tiny deviations from cubic structure even in its ground state.

The coupling between electronic and lattice degrees of freedom is an essential ingredient of correlated electron physics and inevitably manifested in many of the related phenomena. The representative examples, when the 2 degrees of freedom indeed show cooperative orderings, range from the highlighted family of ferroelectrics [1] through materials exhibiting the cooperative Jahn-Teller effect [2] to systems with spin Peierls [3], and a charge and/or spin density wave ground state [4]. Perhaps the most delicate pattern, where all the orbital, charge, spin, and lattice degrees of freedom are interlocked, is realized in manganites being the mother state for the colossal magnetoresistance effect [5]. No less common and fundamental are the various manifestations of the electron-phonon coupling in the charge transport such as the conventional superconductivity, the polaron motion in bad metals [6], or the Fano asymmetry of optical phonon modes [7].

The interaction between spin and lattice degrees of freedom has been attracting a lot of interest both in the context of magnetoelastic effects [8] and as a possible path to get rid of the ground state degeneracy in frustrated magnets [9,10]. It is generally expected that a symmetry breaking magnetic order can in principle change the underlying lattice via the spin-lattice coupling. A classic example is the trigonal distortion in the Néel state of MnO, NiO with rocksalt structure where the exchange interactions serve as the primary driving force of the transition and the lowering of the lattice symmetry from cubic to rhombohedral is a subsidiary consequence [11,12].

On the other hand, in highly frustrated antiferromagnets a secondary energy scale, though generally much weaker than that of the spin-spin interaction, can play an essential role in the development of long-range magnetic order.

Such a phenomenon was observed in several ACr$_2$O$_4$ chromite spinels with nonmagnetic A-site ions and termed as the spin Jahn-Teller effect [9,10]—being analogous to the ordinary Jahn-Teller effect when the orbital degeneracy of an ion is lifted by the lowering of the crystal symmetry. In these spinels, the frustration of $J_{\text{Cr-Cr}}$ antiferromagnetic nearest neighbor interaction on the corner sharing network of Cr^{3+} tetrahedra, the so-called pyrochlore structure, is eliminated by a tetragonal distortion of the lattice. This releases the frustration and a unique antiferromagnetic ground state appears. Beyond the static structural distortion, the anisotropy of the lattice dynamics (i.e., considerable splitting of some infrared active phonon modes) upon the antiferromagnetic transition has attracted interest as a consequence of the strong spin-phonon coupling [9,13,14].

In this Letter, we study representatives from another class of spinel compounds where the A^{2+} ions forming a diamond lattice are also magnetic, namely, CoCr$_2$O$_4$, FeCr$_2$O$_4$, and CuCr$_2$O$_4$. If the $J_{A\text{-Cr}}$ coupling between the A site and the Cr^{3+} $S = 3/2$ spins becomes large enough, it helps to overcome the frustration of the pyrochlore lattice and may result in a complex noncollinear order with three magnetic sublattices [15]—A, Cr$_1$ and Cr$_2$ as displayed in Fig. 1(a). Conical spin structure was indeed observed in CoCr$_2$O$_4$ and FeCr$_2$O$_4$ below $T_S = 27$ K and 35 K, respectively [16–18]. Though ferrimagnetic order is already present above the conical phase—below $T_C = 93$ K and 97 K for A = Co and Fe—the spin components perpendicular to the spontaneous magnetization are still disordered [17]. On the other hand, CuCr$_2$O$_4$ becomes a canted antiferromagnet at $T_C = 152$ K with again three magnetic sublattices [19].
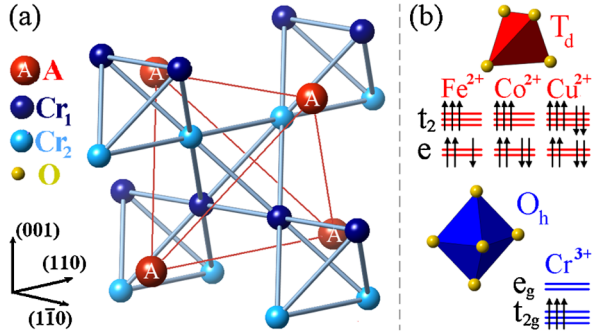
FIG. 1 (color online). (a) Representative part of the spinel structure with Cr^{3+} ions forming a pyrochlore and A^{2+} ions a diamond lattice. ACr_2O_4 chromites with magnetic A-site ions (Fe, Co, and Cu)—irrespective of the details of the spin order—contain three magnetic sublattices A, Cr^1, and Cr_2 in their ferrimagnetic phase [23]. The net magnetization points along one of the main cubic axes with the Cr_1 and Cr_2 chains running in the normal plane being also perpendicular to each other. (b) Occupation of the crystal-field levels for Fe^{2+}, Co^{2+}, Cu^{2+}, and Cr^{3+} in the cubic phase of ACr_2O_4.

$CoCr_2O_4$ has no orbital degree of freedom since the ground state of both the Co^{2+} ($3d^7$) and Cr^{3+} ($3d^3$) ions is an orbital singlet due to the tetrahedral and octahedral crystal field, respectively [see Fig. 1(b)]. Accordingly, this compound is reported to retain its cubic spinel structure down to low temperatures ($T = 10$ K) with the space group $Fd\bar{3}m$ [15,18]. In $FeCr_2O_4$ and $CuCr_2O_4$ the A-site ions are Jahn-Teller active: The high-temperature orbital degeneracy indicated in Fig. 1(b) is lifted by a tetragonal distortion at $T_{JT} = 135$ K and $T_{JT} = 850$ K, respectively [20,21]. The factor group analysis yields four infrared active T_{1u} modes in a cubic spinel. When the symmetry is reduced to tetragonal (D_{4h} point group), we should find that triple degenerate T_{1u}'s split into a singlet and a doublet, $T_{1u} = A_{2u} \bigoplus E_u$ [22]. For further lowering of the symmetry to orthorhombic (D_{2h} point group), the degeneracy of the modes is fully lifted according to $T_{1u} = A_{2u} \bigoplus B_{1u} \bigoplus B_{2u}$, and 12 infrared active lattice vibrations are expected in the spectrum.

Our primary goal was to follow the signatures of the magnetic transitions on the lattice dynamics by infrared spectroscopy. We succeeded in observing the splitting of several modes, pointing out that the spin ordering does reduce the symmetry of the lattice, as well.

Single crystals of $CoCr_2O_4$ and $FeCr_2O_4$ were grown by chemical vapor transport while $CuCr_2O_4$ was prepared by a flux decomposition method [23]. Reflectivity spectra, both polarized and unpolarized, were measured with microscopes on the as-grown surfaces ([111] for $A =$ Co, Fe and [010] for $A =$ Cu) between $T = 10$ and 300 K. Although our focus is on the lattice vibrations in the far-infrared region, we have carried out the experiments over a broad energy range ($\omega = 100$–$320\,000$ cm^{-1} and $\omega = 100$–$40\,000$ cm^{-1} at room and low temperatures, respectively) to facilitate the proper Kramers-Kronig transforma-

tion. Throughout the Letter, the photon frequency is given in wave number units corresponding to the choice that the velocity of light is taken to unity.

Low-temperature optical conductivity spectra of the ACr_2O_4 spinels are shown in Fig. 2 in the range of the optical vibrations. Complex optical conductivity is related to the dielectric constant according to $\sigma(\omega) = [\epsilon(\omega) - 1]\omega/4\pi i$; thus, its real part describes the absorption of light in matter. Only four phonon modes are discernible in the spectra of $CoCr_2O_4$. In contrast, each T_{1u} mode of $CuCr_2O_4$ is split, and the lowest-energy mode in $FeCr_2O_4$ also has a multipeak structure indicating symmetry lowering in its originally cubic spinel structure. For a rigorous analysis we have fitted the optical conductivity as a sum of Lorentz oscillators,

$$\sigma(\omega) = \frac{\omega}{4\pi i}\left(\epsilon_\infty - 1 + \sum_i \frac{S_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i}\right), \quad (1)$$

where S_i, ω_i, and γ_i are the oscillator strength, the frequency, and the damping rate of the modes and ϵ_∞ is the high-frequency dielectric constant. In $CuCr_2O_4$, we observed the large splitting ($\Delta\omega \approx 50$ cm^{-1}) of each T_{1u} mode into a doublet and a singlet at room temperature as the consequence of the cooperative Jahn-Teller distortion below $T_{JT} = 850$ K. The lifting of degeneracy for the lowest- and highest-energy mode in $FeCr_2O_4$ is similarly observed below $T = 150$ K in accordance with $T_{JT} = 135$ K, while the two middle phonon lines only show anomalous shift below this temperature. The temperature dependence of the phonon frequencies can be followed in Fig. 3.

We found that the modes, whose degeneracy is partly lifted by the tetragonal distortion in $FeCr_2O_4$ and $CuCr_2O_4$, exhibit further splitting at the ferrimagnetic transition. This magnetically induced splitting is well-resolved for each of these phonon lines, being as large as $\Delta\omega/\omega_0 \approx 10\%$ for the lower-energy ones. Furthermore, in $FeCr_2O_4$ the ferroelectric transition is accompanied by a sudden hardening of the phonon modes originating from $T_{1u}(1)$. The sequence of the mode splittings upon T_{JT} and
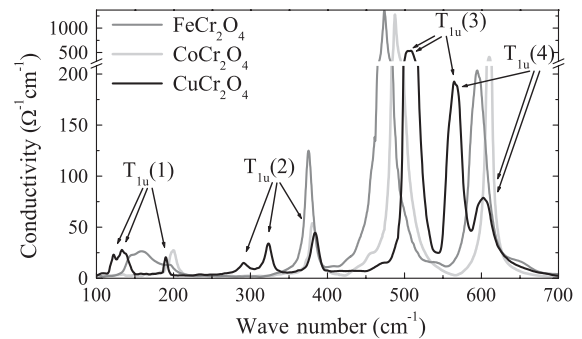

FIG. 2. Real part of the optical conductivity spectrum for $FeCr_2O_4$, $CoCr_2O_4$, $CuCr_2O_4$ at $T = 10$ K in the range of infrared active phonons. Arrows indicate the splitting of the threefold degenerate T_{1u} modes in $CuCr_2O_4$.
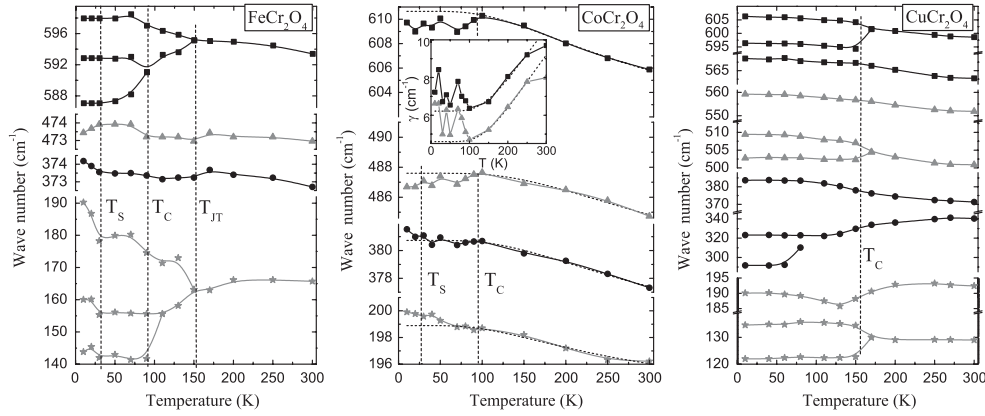
FIG. 3.   Temperature dependence of the phonon frequencies in $FeCr_2O_4$, $CoCr_2O_4$, and $CuCr_2O_4$. T_{JT}, T_C, and T_S represent transitions to the tetragonal, ferrimagnetic, and conical spin state, respectively. Modes originating from the same T_{1u} are labeled by common symbols. The inset shows the damping rate of two modes in $CoCr_2O_4$. Dashed lines fitted to the high-temperature part of the $\omega_i(T)$ and $\gamma_i(T)$ curves indicate the conventional anharmonic behavior due to phonon-phonon scattering [14].

T_C is exemplified in Fig. 4 by the temperature dependence of the second mode in $CuCr_2O_4$. The polarization dependence of the spectra over the same region proves that the structural distortion is a static, long-range one and both the structural and magnetic domain sizes exceed the spot size of ~ 100 μm used in our measurements.

Though we could not resolve any splitting of the phonon lines in $CoCr_2O_4$, the damping rate γ of the two higher-energy ones seemingly shows a remarkable increase upon the magnetic ordering as followed in the inset of the middle panel of Fig. 3. (The same is valid for the third mode in $FeCr_2O_4$ at T_{JT} and T_C, as well.) This is in strong contrast with the conventional behavior characteristic of all the other modes where the damping rate either follows a monotonic decrease in accordance with the freezing out of phonon-phonon scattering or even exhibits a sudden drop upon the transition due to the vanishing of spin-phonon scattering in the magnetically ordered phase. Therefore, this anomalous enhancement is likely the signature of tiny splittings ($\Delta\omega \approx 1$–2 cm^{-1}) mostly masked by the large damping rates.

The complete lifting of phonon degeneracy in $CuCr_2O_4$ and $FeCr_2O_4$ according to $T_{1u} \rightarrow A_{2u} \bigoplus B_{1u} \bigoplus B_{2u}$ gives evidence for the magnetically induced lowering of the lattice symmetry at least to orthorhombic. The corresponding D_{2h} point group is fully compatible with the crystal structure shown in Fig. 1(a) with the following assumptions: Cr_1 and Cr_2 sites are necessarily distinguishable in the sense that magnetic quantities and spin-lattice coupling can transmit this nonequivalence to primarily spin-independent (or spin integrated) properties such as crystal structure, lattice dynamics, dielectric response, etc. On this basis, the lattice symmetry in the magnetic phase of $CoCr_2O_4$ should also be reduced to orthorhombic though the associated distortion is very weak [24]. The lack of any observable change in the lattice dynamics upon the ferroelectric transition is rather surprising and implies that the conical spin order alone can induce ferroelectricity without strong electron-lattice coupling. On the other hand, the

large mode splitting ($\Delta\omega/\omega_0 \approx 10\%$) observed in the other two materials implies that spin-phonon coupling is indeed strong in these cases.

Former optical studies on chromite spinels with non-magnetic A-site ions have found noticeable splitting only for the two lower phonon resonances upon the magnetic transition except for $ZnCr_2S_4$ where the effect is almost equally manifested in each mode [14]. These findings were interpreted in terms of the spin-phonon interaction coming from the spatial dependence of the exchange couplings [9,13,14]. Microscopic models explained the large splitting of the two lower-energy T_{1u} modes, showing that the corresponding vibrations mostly affect the Cr-Cr bonds responsible for the nearest neighbor antiferromagnetic interaction. In these highly frustrated magnets the long-range spin order can only be established by the spin Jahn-Teller effect; thus, magnetic ordering and structural distortion are necessarily interlocked.

This scenario does not apply for the present spinels. At first, they order at higher temperatures, indicating the
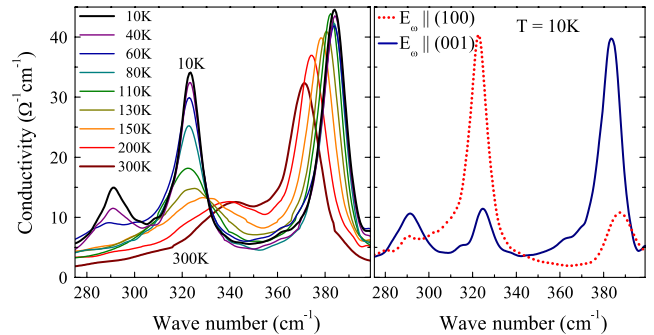

FIG. 4 (color online).   Optical conductivity of $CuCr_2O_4$ in the range of the second phonon mode at various temperatures. The splitting induced by the cooperative Jahn-Teller effect is already present at room temperature, while a third, low-energy peak becomes isolated only in the magnetic phase. $T = 10$ K polarized spectra with $\mathbf{E}_\omega$ roughly parallel to the tetragonal axis (001) and along (100) are plotted in the right panel.

release of frustration due to the coupling between spins on the pyrochlore and the diamond lattice. With the Jahn-Teller active ion on the A site, frustration can be further reduced as manifested in the high T_C of $CuCr_2O_4$ which has the strongest tetragonal distortion among the ACr_2O_4 family. Here, we report distinct differences in their vibrational properties. In $CuCr_2O_4$ and $FeCr_2O_4$, besides the splitting of lower-energy modes we found that the degeneracy is lifted for the higher-lying ones, as well. (Hints of splitting in $CoCr_2O_4$ appear in the third and forth modes, as well.) This behavior can be explained by the additional antiferromagnetic A-O-Cr superexchange which is thought to be relevant beyond the antiferromagnetic Cr-Cr direct exchange and the ferromagnetic Cr-O-Cr superexchange existing for the nonmagnetic A site [15]. Lattice dynamical calculations on $MgTi_2O_4$ [25] and $ZnCr_2O_4$ [13] predict that $T_{1u}(3)$ and $T_{1u}(4)$ vibrations have strong contributions from oxygen displacements. Thus, they can effectively modulate the A-O-Cr and Cr-O-Cr exchange path. Since the spins on Cr_1 and Cr_2 sublattices "align antiparallel," the latter has minor significance, and we attribute the magnetically induced lattice distortion to the spin-phonon coupling corresponding to the A-O-Cr exchange path.

There is another possible scenario where the interplay of the Jahn-Teller effect and spin-orbit coupling on the A-site ions plays a crucial role. This is supported by the remarkable contrast between $CoCr_2O_4$ with nearly isotropic lattice dynamics and $CuCr_2O_4$ in which each phonon mode exhibits pronounced splitting. In the former, the orbital moment of Co^{2+} ion is quenched and the spin-orbit interaction is weak since it can only mix states separated by the large tetrahedral crystal field, while in $CuCr_2O_4$ the spin-orbit interaction is more effective as it competes only with the smaller tetragonal component of the crystal field within the t_2 subspace [see Fig. 1(b)]. This possibility should be theoretically investigated as an alternative way to introduce spin-lattice coupling besides the spatial variation of the exchange interactions considered so far in spinels with the nonmagnetic A site.

Another peculiarity of these compounds is that magnetic ordering is strongly manifested in the lattice dynamics while it is hardly observable in static distortions. Though no structural component of the magnetic transition has been found so far in x-ray and neutron scattering experiments, we could clearly demonstrate the lowering of the crystal symmetry by the analysis of infrared active phonon modes. The only compound, related to this family, where the onset of a magnetically induced tetragonal to orthorhombic distortion was reported at $T_C = 74$ K is $NiCr_2O_4$ [26]. This tiny orthorhombic distortion ~0.18% falls far below the scale of the tetragonal one, being ~5%. The latter is induced by the Jahn-Teller effect at $T_{JT} = 320$ K, similarly to the case of $FeCr_2O_4$ and $CuCr_2O_4$, where its size is ~2.5% and ~10%, respectively. Phonon modes turn out to be better indicators of the structural transformation, as well, since some of the mode splittings in $CuCr_2O_4$ reach $\Delta\omega/\omega_0 \approx 40\%$.

In conclusion, we pointed out that in ACr_2O_4 spinels with a magnetic ion on the A site, the lattice symmetry is broken upon their ferrimagnetic transition. The detailed analysis of the infrared active phonon modes showed that in $CuCr_2O_4$ and $FeCr_2O_4$ the lattice form is lowered to orthorhombic from originally tetragonal in their high-temperature paramagnetic phase. We found that the second magnetic transition of $FeCr_2O_4$ also affects the lattice vibrations. In contrast, $CoCr_2O_4$ shows tiny deviation from the cubic structure down to $T = 10$ K.

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