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Orbital dimerization in $NaTiSi_2O_6$. An orbital analogue of the spin-Peierls phase transition

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Abstract

The phonon dynamics in $NaTiSi_2O_6$ is studied using the Raman scattering technique. The observed phonon anomalies around $T = 210$ K combined with theoretical considerations show that the high-temperature dynamical Jahn–Teller phase of $NaTiSi_2O_6$ exhibits a spontaneous breaking of translational symmetry into an orbital dimerized state. We describe this phase instability as an orbital analogue of the spin-Peierls phase transition.

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In strongly correlated transition-metal compounds the interplay between spin, charge and orbital degrees of freedom, combined with their coupling to the lattice, gives rise to a wealth of possible spin, charge and orbital orderings [1]. Systems with orbital degeneracy are particularly interesting because orbitals couple to the lattice via the cooperative Jahn–Teller (JT) effect on one hand, and via superexchange interactions to the electronic spin on the other hand [2]. Therefore, at an orbital ordering (OO) phase transition the magnetic susceptibility and phonon properties will be affected at the same time. Here we analyze a new type of ordering and the phase transition which is discovered in $NaTiSi_2O_6$. This compound is rather different from other pyroxenes as it lacks low-temperature antiferromagnetic (AF) order, and shows signs of the opening of a spin gap instead (its magnetic susceptibility sharply decreases below 210 K) [3].

In the Raman scattering spectra of $NaTiSi_2O_6$, Fig. 1, we find a dramatic change in the phonon properties around 210 K, which coincides with the temperature where the abrupt drop of the magnetic susceptibility is observed. Some typical temperature dependencies of the phonon frequencies and line widths are shown in the insets of Fig. 1. The modes at 221 and 209 cm^{-1} exhibit an anti-crossing behavior which indicates that a phonon symmetry change below T_c. Next, the mode at about 946 cm^{-1} softens by about 10 cm^{-1}, while the mode at 966 "splits", and hardens by 25 cm^{-1}. Existence of large phonon anomalies at the temperature which coincides with T_c obtained from susceptibility measurements [2] indicates that *magnetic ordering is accompanied with a structural phase transition*, just as one would expect for a canonical OO transition. The full-width at half-maximum (FWHM) of the 946 cm^{-1} phonon increases up to the maximum value at about 210 K, and then decreases to the saturation value which is much smaller then the $T = 300$ K value, the right inset of the top panel in Fig. 1. This implies that *bond fluctuations are considerably larger in the high-T than in low-T phase* and emphasizes the orbital character of disorder at high-T [4].

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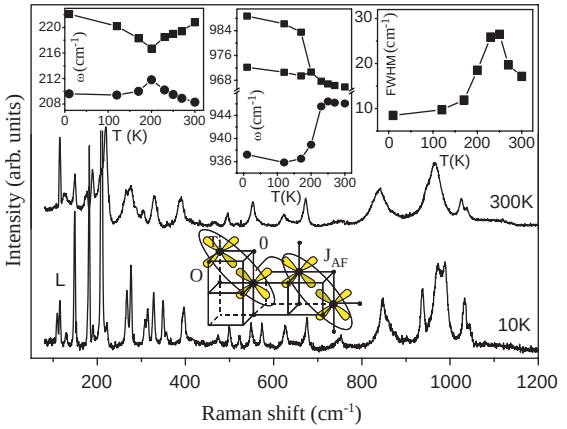

Fig. 1. Raman spectra of $NaTiSi_2O_6$ at 300 K (upper panel) and 10 K (lower panel). Upper left and middle insets: frequency vs. temperature for various phonons. Upper right inset: FWHM vs. temperature for 946 cm^{-1} mode. Lower inset: schematic representation of the orbital dimers.

$NaTiSi_2O_6$ belongs to the pyroxene family, with a structure that consists of isolated quasi one-dimensional chains of edge-sharing TiO_6 octahedra. This structure has a magnetic moment corresponding to $S=\frac{1}{2}$ (Ti^{3+}), and *active* t_{2g} orbitals (splitting of t_{2g}'s due to non-cubic crystal fields is smaller than typical hopping integrals) [5]. The low-energy electronic properties are governed by the three-fold degenerate t_{2g} states, and the problem is further reduced by considering the symmetry allowed hopping paths in the chain geometry, see inset in low panel Fig. 1. The Hamiltonian is

$$H=|J|\sum_{i,j}\mathbf{S}_i\cdot\mathbf{S}_j\left[\frac{1}{4}+T_i^zT_j^z+\frac{(-1)^i}{2}(T_i^z+T_j^z)\right], \qquad (1)$$

where we use the orbital operators T ($T_i^z=\frac{1}{2}$ corresponds to an occupied $|xy\rangle$ orbital and $T_i^z=-\frac{1}{2}$ to an occupied $|yz\rangle$ orbital on site (i)), and i,j are neighboring sites. The $|xz\rangle$ orbitals are non-bonding and can be considered inert on this level of approximation. The ground state of the Hamiltonian is clearly a *ferro-orbital* state, with spin-singlets on each bond, where the energy per dimer is $-3J/4$. At $T=0$ the system is condensed into an orbital-dimer state and the translation symmetry is broken. This explains the structural change at T_c, e.g. the symmetry change and the energy shifts of the phonon excitations in the Raman spectra of $NaTiSi_2O_6$ and the observation of a large spin gap [2]. At high-T, due to strong orbital-lattice coupling and JT effect, the orbital fluctuations lead to a homogeneous exchange along the chain, and induce large phonon broadenings. In that respect the high-T phase of $NaTiSi_2O_6$ resembles a *dynamical JT phase*. The spin fluctuations above the OO temperature are AF since the long-range order is absent in the orbital sector (a mean-field approximation for the Hamiltonian gives for the expectation values $\langle T_i^z\rangle=0$, and $|\langle T_i^zT_j^z\rangle|<\frac{1}{4}$) [5]. We conclude that the phase transition in $NaTiSi_2O_6$ corresponds to an orbital order–disorder phase transition with appropriate concomitant magnetic and lattice changes. Finally, this phase instability can be described as an *orbital analogue of the SP phase transition*.

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