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Raman spectroscopy of $Na_3Co_2SbO_6$

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Materials, in which competition of a bond-directional exchange interaction leading to a strong frustration presented, can be a physical realization of the Kitaev model described by the Hamiltonian

$$H = \sum_{\langle ij \rangle_\gamma} K^\gamma \hat{S}_i^\gamma \hat{S}_j^\gamma, \qquad (1)$$

where different spin components $\gamma = \{x, y, z\}$ for three symmetry inequivalent nearest neighbours (numerated by site indexes i and j) on the honeycomb lattice turn out to be coupled by the exchange constants K^γ [1]. Such materials are under active investigation nowadays [2–4]. An efficient method of studying such Kitaev materials is the Raman spectroscopy.

In the paper we for the first time present the results of Raman measurements in a wide frequency range for one of the honeycomb cobaltites $Na_3Co_2SbO_6$ considered as possible candidates for Kitaev physics as well as the density functional theory (DFT) lattice dynamics simulations for the compound.

Co, forming here a layered honeycomb structure, is 2+ with electronic configuration $3d^7$ and spin $S = 3/2$. The magnetic ground state corresponds to a so-called antiferromagnetic (AFM) zigzag structure, when ferromagnetic (FM) spins are ordered in zigzag fashion [5]. Effective magnetic moment is $5.2 - 5.5\mu_B$ [5–7], suggesting substantial contribution of the orbital moment.

Although $Na_3Co_2SbO_6$ orders magnetically it was recently shown that a moderate magnetic field of 1–2 T suppresses the long-range magnetic order and leads to a field-induced state, which can retain some features of Kitaev physics [8].

Polarized Raman measurements in the temperature range of 80 to 300 K were performed in backscattering geometry from the polycrystalline sample [8] using an RM1000 Renishaw microspectrometer.

DFT + U calculations ([9], $U = 7$ eV, $J_H = 1$ eV, [10, 11]) have been performed using VASP [12] within generalized gradient approximation (GGA) [13]. Phonon frequencies at Γ-point were computed using the density functional perturbation theory (DFPT) [14, 15].

$Na_3Co_2SbO_6$ crystallizes in a monoclinic structure (space group C2/m) [5], which implies $7A_g$ and $8B_g$ phonons, that theoretically can be observed with Raman spectroscopy. The measured room temperature spectra show 11 lines at frequencies 121, 159, 207, 292, 371, 444, 495, 528, 543, 618, and 636 cm^{-1} (see Fig. 1). The exact shape of phonon lines is difficult to determine due to their large width and the overlap of some lines with others for the power sample.

As the temperature decreases, most of the lines narrow only slightly; the accompanying hardening suggests the influence of anharmonic contributions. The new narrow peak appears below 200 K at 525 cm^{-1} (see the insert in Fig. 1a). As there is no information about structural transitions at this temperature in $Na_3Co_2SbO_6$, it can be a sign of either two-magnon scattering or a gradual development of the short-range correlations with decreasing temperature.

In the high-frequency region, the spectra show broad bands at 1060, 1570 and possibly 2080 cm^{-1} given in the insert in Fig. 1b. Such extra peaks are typical for some other honeycomb lattice layered compounds and associated with high-order phonon scattering.

It turned out that taking into account spin degrees of freedom in DFT + U calculations strongly affects the resulting phonons frequencies and hence, their agreement with the experimental ones. It can be regarded as a proof of the sensitivity of the phonons to magnetic

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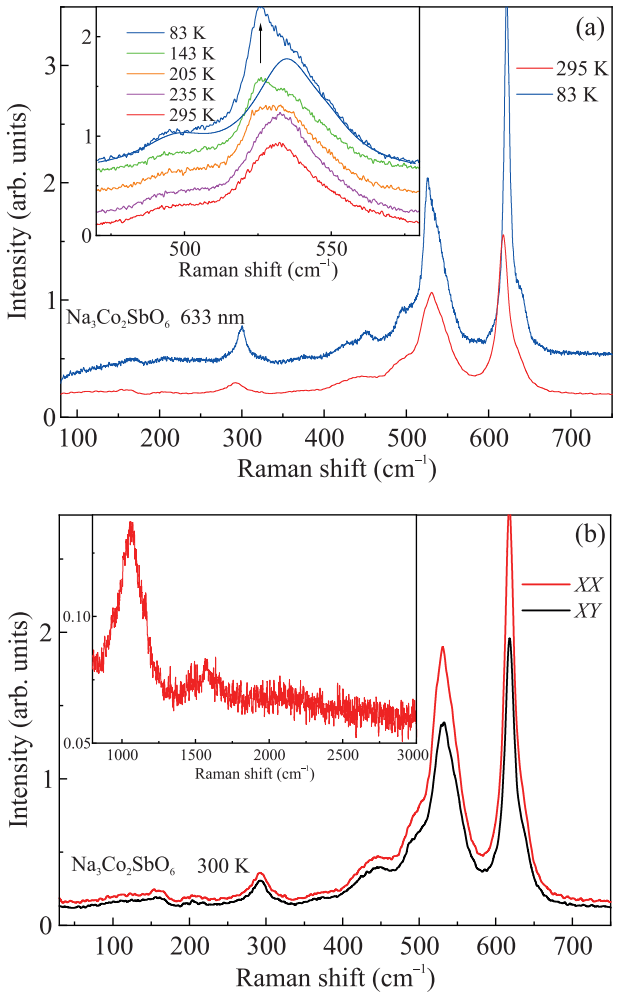

Fig. 1. (Color online) (a) – Raman spectra of $Na_3Co_2SbO_6$ measured at 83 and 295 K. Insert shows temperature evolution of the spectral range where line near 525 cm^{-1} appears. (b) – Raman spectra of $Na_3Co_2SbO_6$ measured in XX and XY scattering geometries at 300 K. High-frequency spectral range containing two-phonon excitation is shown in insert

order in the compound and highlights the importance of the spin-lattice coupling in $Na_3Co_2SbO_6$.

Considering of the spin-orbit coupling (SOC) also slightly modifies the calculated phonon spectrum and further improves agreement with the experiment, especially for the highest-frequency modes.

The effect of both magnetism and SOC is mostly observed for the highest phonon modes. According to the results of our calculations the two highest modes correspond to stretching distortions of SbO_6 octahedra, which are in the centers of Co hexagons. In case of AFM zigzag order magnetostriction leads to decrease of Sb-Co distances. This explains frequency growth and, hence, hardening of the stretching mode.

Finally, the Raman spectra do not reveal formation of high-energy continuum observed in some Kitaev materials [16, 17].

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