

Raman spectra of a misfit layered $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystal

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The polarized Raman spectra have been measured on misfit layered $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystal, with the temperature range of 9–300 K. Nine phonon modes have been found in parallel polarization configurations and six in cross polarization configurations. The frequencies of the phonon modes related to the vibration of oxygen atoms show anomalous temperature dependence below the metal-insulator transition temperature 50 K (T_c). It is discussed in terms of spin-phonon coupling and the reorganization of the electronic states below T_c .

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I. INTRODUCTION

Transition-metal oxides have attracted a lot of interest since the discovery of high-temperature superconductivity in layered cuprates. Recently, more attention has been paid to cobalt oxides because of their large thermopower and the discovery of superconductivity in the hydrated cobaltate $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$.^{1–3} A series of quasi-two-dimensional cobalt oxides such as Na_xCoO_2 , $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$, etc., have been synthesized and widely studied. These compounds are characterized by a CoO_2 triangular-lattice layer consisting of edge-shared CoO_6 octahedra.

Although with the similar CoO_2 triangular layer, unlike Na_xCoO_2 , the crystal of $\text{Ca}_3\text{Co}_4\text{O}_9$ has a monoclinic misfit layered structure, which belongs to the space group $C_{2/m}$ ($Z=6$).⁴ It is composed of alternating stacking structure along the c axis of a distorted Ca_2CoO_3 rocksalt (RS)-like layer and a CdI_2 -type CoO_2 layer. These two layers have similar a , c , and β lattice parameters but different b parameters. To emphasize the incommensurate nature of the structure, $\text{Ca}_3\text{Co}_4\text{O}_9$ can be denoted as $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{(b1/b2)}$ or $[\text{Ca}_2\text{CoO}_3]_{(b2/b1)}[\text{CoO}_2]$, where $b1$ and $b2$ are two different lattice parameters for the RS subsystem and the CoO_2 subsystem, respectively.

Theoretical and experimental studies on $\text{Ca}_3\text{Co}_4\text{O}_9$ were limited due to the complicated misfit layered structure. So far, experimental studies of transport, thermodynamic, and magnetic properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ have been carried out.^{5–13,16,17} The temperature dependence of the in-plane resistivity (ρ_{ab}) shows a metalliclike behavior as the temperature decreases from 300 to 50 K. However, an insulatinglike behavior in ρ_{ab} was observed below 50 K.¹² A positive Hall resistance (R_H) observed in this crystal implies that the charge carriers are holelike. It exhibits a strong temperature dependence from 100 up to 300 K, with an unusual large increase relative to conventional metals but consistent with the behavior of strongly correlated metals.^{5–8} Moreover, specific heat measurements of sintered samples, which have an enhanced electronic contribution with $\gamma=93 \text{ mJ}/(\text{mol K}^2)$, exhibit the properties of strongly correlated electron system.⁵ Its magnetic characteristics are more complicated than its

transport properties because of the mixed valence state of Co ions in both subsystems. Three magnetic transitions were reported by dc susceptibility measurement: the first is a ferromagnetic transition at 19 K, the second is an incommensurate spin-density-wave transition at 27 K, and the third is a spin state transition around 380 K. The first two transitions can be only observed when the applied magnetic field is perpendicular to ab plane.^{11,13,16,17} Furthermore, a giant negative magnetoresistance (MR) reaching -35% was observed in the ab plane below 50 K.^{9,12} This anisotropic behavior indicated that the alternating stacking structure plays an important role in its magnetic properties. The coexistence of a large thermopower, a low resistivity, and high-temperature stability was also found in $\text{Ca}_3\text{Co}_4\text{O}_9$, which made it a promising candidate for thermoelectric applications.^{18–20} The reason for the good Seebeck coefficient of this material coexisting with metallic properties and the anomalous properties listed above is not well known yet.

Raman scattering, as an inelastic light-scattering experiment, is a unique technique for studying lattice vibrations, which is one of the most important elementary excitations in solids. The understanding of most structural, electronic, and magnetic properties is based on the knowledge of lattice vibrations. In this paper, we present the polarized Raman scattering measurements on oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystal at various temperatures. Several phonon modes were observed in the polarized Raman spectra. An unusual change of some phonon frequencies was found near the metal-insulator transition temperature of 50 K, which was considered to be related to spin-phonon coupling or reorganization of electronic states.

II. SAMPLE AND EXPERIMENT

The single crystal of $\text{Ca}_3\text{Co}_4\text{O}_9$ was prepared by the solution method using $\text{K}_2\text{Co}_3\text{-KCl}$ as fluxes with the composition of 4:1. CaCO_3 and Co_3O_4 powders of reagent grade were thoroughly mixed in the Ca:Co ratio of 3:4 with total weight of 10 g. The mixture was preheated at 1173 K for 20 h and then mixed with 80 g flux. The powder was then melted at 1223 K and soaked for 20 h, and finally cooled

down to 873 K at a rate of 6 K/h. The grown samples were washed with hot distilled water to remove the flux. These crystals were annealed at 723 K in an oxygen gas flow for 12 h, and then cooled down to room temperature. The finally obtained single crystals were thin platelets with typical dimensions of $4 \times 5 \times 0.1$ mm³. An x-ray diffraction study indicated that the growth surface of the platelets was the *ab* plane, and both optical microscope and scanning electron microscopy observations showed that the platelets have an aligned stack along the *c* axis, with randomly rotated *ab* planes. The preparation and characterization of the samples were reported in greater detail elsewhere.⁹⁻¹¹

A fine surface was obtained after the sample was cleaved. The crystal was oriented by x-ray Laue diffraction, just before it was mounted on the cold finger in the cryostat. Raman spectra were measured with the 514.5 nm line of an argon ion laser (Spectra-Physics 2017). The laser excitation was focused onto a spot less than 70 μ m in diameter, and the power was stabilized at 6 mW in order to reduce the laser heating. The rise of temperature caused by laser illumination is less than 10 K. The Optistat^{CFV} cryostat (Oxford Instruments) with a vacuum of about 10^{-7} Torr can provide a temperature range from 2 to 300 K using liquid helium as its cooling source. Scattered light was collected in the pseudo-backscattering geometry. A U1000 (Jobin-Yvon) double-grating monochromator and a back-illuminated charge coupled device cooled by liquid nitrogen were used to disperse and detect the scattered light, respectively.

In the present study, Stokes shifted Raman spectra were measured between 150 and 1100 cm⁻¹ in the *xx* and *xy* scattering geometries, where *x* denotes the (1,0,0) direction and *y* the (0,1,0) direction, with respect to the principal axes of crystal. The polarization for the incoming and outgoing photons was always parallel to the *ab* plane of the sample.

III. RESULTS AND DISCUSSION

The *xx* and *xy* polarized Raman spectra of Ca₃Co₄O₉ measured at the nominal temperature from 9 to 300 K are shown in Figs. 1(a) and 1(b), respectively. In the *xx* spectra, one can observe nine Raman peaks located at about 180, 300, 358, 440, 545, 568, 630, 660, and 685 cm⁻¹, respectively. The *xy* spectra exhibit six peaks, five of which appearing at about 177, 360, 447, 550, and 655 cm⁻¹. The 300, 568, 630, and 685 cm⁻¹ peaks presented clearly in the parallel polarization are not seen in the cross polarization, whereas new peaks appear near 428 cm⁻¹ in the latter configuration.

In the *xx* polarized Raman spectra, the frequencies of the peaks located at 300, 358, and 630 cm⁻¹ increase dramatically when the temperature is down to about 50 K. The detailed changes are summarized in Fig. 2. The reason for these anomalous changes is discussed later. In the *xy* spectra, a peak splitting can be observed around 450 cm⁻¹, the origin of which is not known yet. The asymmetry of the peak at about 550 cm⁻¹ might be an indication of electron-phonon coupling.

To further understand the Raman peaks observed in the spectra and the differences between two polarizations, the corresponding Raman tensors and expected intensities in the

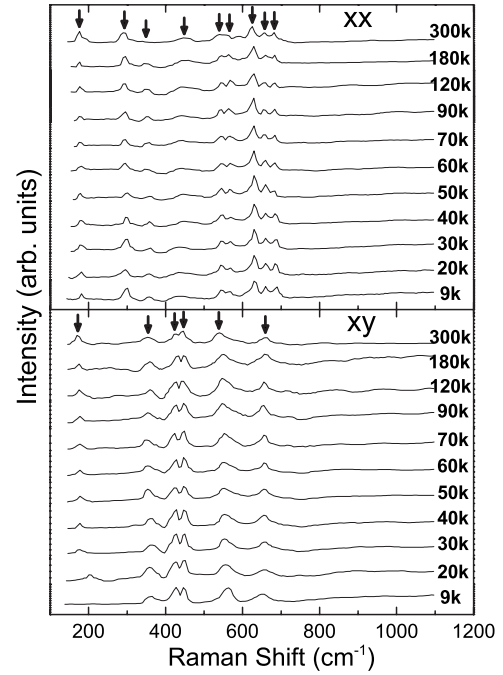


FIG. 1. Raman spectra of Ca₃Co₄O₉ single crystal measured from 9 to 300 K with *xx* and *xy* polarization. The spectra have a systematic offset to arrange one above another to give a legible comparison of different temperatures. Each peak is marked by an arrow in the spectra measured at 300 K.

xx and *xy* scattering configurations are presented in Table I. As we can see, the *A_g* modes are expected to appear in both the parallel *xx* scattering configuration and the cross *xy* configuration, whereas the *B_g* modes cannot be seen in neither *xx* nor *xy* polarization.

Due to its complicated misfit structure and the lack of relative experimental and theoretical data, an assignment of

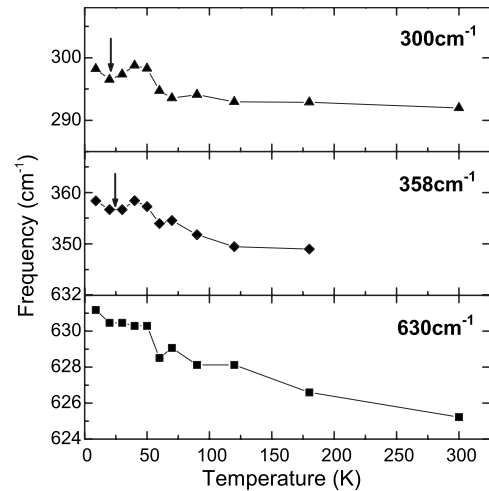


FIG. 2. Temperature dependence of the position of three *xx* polarization Raman peaks of Ca₃Co₄O₉ single crystal. It can be observed that notable changes of the phonon frequencies arise at about 50 K. Moreover, other changes take place in the two lower frequency phonon modes when the temperature is below 25 K, as indicated by the arrows.

TABLE I. The corresponding Raman tensors and expected intensities in the xx and xy scattering configurations.

Scattering configuration	Raman tensor		Expected Raman intensities	
	$A_g \rightarrow \begin{bmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{bmatrix}$	$B_g \rightarrow \begin{bmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{bmatrix}$	A_g	B_g
xx			d^2	0
xy			d^2	0

the Raman peaks to definite modes is difficult at present. Further detailed study on this crystal such as first-principles calculations should be helpful. However, considering the difference of atomic masses of the three kinds of elements in the crystal, it is reasonable to assign most of the phonon modes observed here to lighter oxygen atomic vibrations, whereas those at lower frequencies are related to the motions of Ca and Co atoms, since the modes of heavy atoms are thought to appear at lower frequency. Newly reported Raman scattering in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ has showed some evidence for the opinion,²¹ which has the same triangular CoO_2 layers as $\text{Ca}_3\text{Co}_4\text{O}_9$.

Figure 2 shows the temperature dependence of the frequencies of three xx polarization Raman peaks. When the temperature decreases from 300 to about 60 K, the frequencies of peaks at about 358 and 630 cm^{-1} are slightly increased, which can be interpreted as mode hardening due to the thermal effect, while the 300 cm^{-1} peak is nearly temperature independent. However, below 50 K, the peaks harden remarkably. It was believed that the usual lattice contraction upon cooling is not mostly responsible for the large (up to 8 cm^{-1}) phonon hardening in such a short temperature range. Moreover, the temperature dependence of frequencies of two phonon peaks at about 300 and 358 cm^{-1} shows an obvious dip at around 20 K, which may be related to the ferrimagnetic transition at this temperature.^{11,16}

It was reported that a large negative MR reaching -35% appears in the ab plane when the temperature is well below 50 K, while the MR in the c plane is only -5% at most.¹² Furthermore, in-plane resistivity measurements for single crystal also showed a metal-insulator transition close to this temperature, while the temperature dependence of the out-of-plane resistivity indicates a semiconductinglike behavior.^{5,12} As it is mentioned above, the large anisotropic properties of this crystal can be apparently related to its two-dimensional layered structure, since the Co-O layers are thought to be an essential part of its transport properties and the interlayer coupling may play an important role in its magnetic characteristic.¹³ So, it is interesting to explore why the remarkable phonon hardening, the large MR, and the metal-insulator transition take place at the same temperature range. It is speculated that the observed frequency shifts in $\text{Ca}_3\text{Co}_4\text{O}_9$ may have something to do with the anomalies of transport properties.

Considering the fact that the negative MR is limited to low-temperature range where the localization occurs, it may be caused by the decrease of spin scattering as a consequence of spin ordering below 50 K. The distinct change of the phonon frequencies vs temperature around T_c may be an indication for a complex mechanism of spin-phonon coupling. The newly reported spin ordered phase transition found in this calcium cobaltite may support this idea.¹³

It is noticed that spin-phonon coupling is usually a small effect in many magnetic systems because the contributions from positive and negative displacements of relevant atoms would be canceled out due to the symmetric vibrations of these atoms. However, in some cases, the coupling is not negligible if the two parts of contributions cannot be canceled. For example, Cu-O planes of most cuprate superconductors are flat. The vibrations of oxygen atoms perpendicular to the Cu-O plane (B_{1g} phonon mode) would have a very small contribution to spin-phonon coupling because the vibrations are symmetric with respect to the two nearest-neighbor Cu²⁺ ions. However, for $\text{YBa}_2\text{Cu}_3\text{O}_x$, it is a little different from other cuprate superconductors because the Cu-O is not flat, but buckling. This means that Cu²⁺ and O²⁻ ions are placed on separate planes. So, the vibrations of oxygen atoms are asymmetric with respect to the two nearest-neighbor Cu²⁺ ions. In this case, spin-phonon coupling is not negligible. In fact, it has been studied in detailed.¹⁴

Another example is Na_xCoO_2 . Like $\text{YBa}_2\text{Cu}_3\text{O}_x$, in this system, cobalt and oxygen ions are also located on separate planes. First-principles calculations on spin lattice have been carried out in this system. The results suggested that the coupling is so strong that it may cause a static magnetoelastic effect, but not a weaker dynamical spin-phonon coupling.¹⁵ Similar Co-O layered structures can be found in the present $\text{Ca}_3\text{Co}_4\text{O}_9$ system compared with Na_xCoO_2 . So, exploring spin-phonon coupling in the system would make some sense based on the above discussions. After all, both spin and lattice are the most important freedoms in the transition-metal oxides.

In a spin ordered state, the superexchange energy J is a function of structural parameters, such as the distance between the magnetic ions and the corresponding angles mediated by the O ions. In other words, it would be modulated by the vibration of relevant ions. For $\text{Ca}_3\text{Co}_4\text{O}_9$, the oxygen and cobalt ions are not in the same plane, just like the cases mentioned above. So, the oscillation of oxygen ions has a strong effect on the magnetic interaction between the neighboring spins on cobalt ions.

In view of the exchange interactions between the nearest-neighbor magnetic atoms, the exchange-dependent term in the Hamiltonian may be given by $H_{ex} = \sum_{i,j} J_{ij}(r_1, r_2, \dots, r_n) S_i \cdot S_j$, where the J_{ij} denotes the exchange energy constant, which is a function of the position coordinates r_n of the oxygen ions in the unit cell. The frequency shift of the phonon that arose from spin-phonon coupling can eventually be expressed as $\Delta\omega = \omega_{ph} - \omega_{ph}^0 = \lambda \langle S_i S_{i+1} \rangle = -\lambda S^2 \phi(T)$. Here, ω_{ph}^0 is the phonon frequency in the absence of spin-phonon coupling, and $\langle S_i S_{i+1} \rangle$ denotes a statistical mechanical average for adjacent spins. S can be taken as 1/2 for $\text{Ca}_3\text{Co}_4\text{O}_9$. $\phi(T)$ is the normalized order

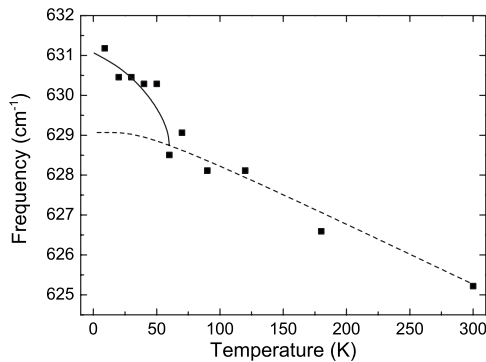


FIG. 3. Frequency vs temperature data for one of xx polarization Raman phonon mode at 630 cm^{-1} . The solid and dashed curves represent the expected behavior with and without spin-phonon coupling, respectively.

parameter defined as $\phi(T) = |\langle S_i S_{i+1} \rangle| / S^2$, which is assumed to be proportional to $\sqrt{1 - T/T_c}$. The spin-phonon coupling coefficient λ can be different for each phonon and can have either sign.^{23–26}

By comparing with the ω_{ph}^0 , we could estimate that values of λ for the 630 cm^{-1} phonon are about -6.8 cm^{-1} (see Fig. 3). This magnitude of λ value is an intermediate one, compared to $|\lambda| \sim 1\text{ cm}^{-1}$ for FeF_2 (Ref. 23) and $|\lambda| \sim 50\text{ cm}^{-1}$ for CuO .²⁶

Another possible reason for the phonon frequency shifts is the reorganization of the electronic states implied by the in-plane resistivity measurement. In view of the electron screening effect, it is possible that local lattice distortion, the

so-called polaron, results in the large frequency shifts. In this scenario, the local lattice distortion due to the strong electron-phonon coupling might change lattice vibrations, which provides a possible explanation for the anomalous shifts. Recent research on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ may provide a sample which shows similar mode hardening due to the strong electron-phonon coupling.²² However, a further study is still required to explain the complex mechanism of electron-phonon coupling.

IV. CONCLUSION

By means of Raman scattering, we have studied the polarized scattering spectra of oriented single crystal $\text{Ca}_3\text{Co}_4\text{O}_9$ over the temperature range from 9 to 300 K. Some phonon frequencies are found to change remarkably around 50 K, where a giant MR and an anomalous transport property were reported previously. The reason for which was discussed in terms of spin and electron couplings. We hope the present work would stimulate the investigation on the novel electronic properties of misfit layered $\text{Ca}_3\text{Co}_4\text{O}_9$.

The present Raman results provide information on lattice vibrations in $\text{Ca}_3\text{Co}_4\text{O}_9$. However, due to its complicated misfit structure, the phonon assignment is impossible by now and the physical origin of its low-temperature anomalies is still unclear. Therefore, more experimental and theoretical studies are needed to explore the material further.

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