



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

Collective versus local Jahn-Teller distortion in $\text{Ba}_{\{3\}}\text{CuSb}_{\{2\}}\text{O}_{\{9\}}$: Raman scattering study

Natalia Drichko, Collin Broholm, K. Kimura, R. Ishii, and Satoru Nakasutji

Phys. Rev. B **93**, 184425 — Published 20 May 2016

DOI: [10.1103/PhysRevB.93.184425](https://doi.org/10.1103/PhysRevB.93.184425)

Collective vs. local Jahn-Teller distortion in $\text{Ba}_3\text{CuSb}_2\text{O}_9$: a Raman scattering study

Natalia Drichko,^{1,*} Collin Broholm,¹ K. Kimura,² R. Ishii,² and Satoru Nakasutji²

¹*Institute for Quantum Matter and Dept. of Physics and Astronomy, Johns Hopkins University, Baltimore MD, USA*

²*The University of Tokyo, The Institute for Solid State Physics, Chiba, Japan*

We present temperature dependent Raman spectra of single crystals of two different samples of spin-orbital liquid candidate $\text{Ba}_3\text{CuSb}_2\text{O}_9$. The “hexagonal” sample is known to show no magnetic order down to low temperatures, while the “orthorhombic” sample undergoes a crossover into an orthorhombic crystal structure below T_{JT} of approximately 200 K and show spin freezing at 110 μK . Our Raman scattering results demonstrate a strong influence of disorder in both samples. The frequencies of stretching vibrations of oxygens associated with CuSbO_9 octahedra indicate a difference in the crystal structure between “hexagonal” and “orthorhombic” samples even at room temperature. On cooling below T_{JT} we observe new bands in the spectra of the “orthorhombic” sample due to a lowering of symmetry of the unit cell and collective Jahn-Teller distortion. The spectra of “hexagonal” sample show that average hexagonal symmetry is maintained at least down to 20 K. An analysis of the band shape of stretching oxygen vibration suggests a weak disordered local Jahn-Teller distortion in the “hexagonal” sample of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ which increases slightly on cooling. This Jahn-Teller distortion is either static or dynamic with frequency below 1.5 THz.

PACS numbers: 74.62.En 78.30.-j

I. INTRODUCTION

Quasi-degenerate states in solids are fertile ground for the emergence of qualitatively new states of matter. One such relevant ground state is a spin-orbital liquid, where orbital degrees of freedom are degenerate. The compound studied in this paper, $\text{Ba}_3\text{CuSb}_2\text{O}_9$ first attracted attention as a candidate for spin-orbital liquid state^{1,2}. Large experimental¹⁻⁵ and theoretical⁶⁻¹⁰ effort is aimed on elucidating the ground state of this material. The important issue for understanding of this system is structural disorder and a tendency to Jahn-Teller (JT) distortion which can be competing with spin-orbital liquid state. Recently, there appeared a theoretical proposal for a spin-liquid state in this material which incorporates disorder and dynamic JT distortion.¹⁰ In our work we were seeking to follow the effects of disorder, as well as possible JT-distortion, in order to add definitive information for understanding of the ground state of $\text{Ba}_3\text{CuSb}_2\text{O}_9$.

In the structure of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ crystals, Cu^{2+} ions are organized into so-called Cu-Sb “dumbbells”, where the atoms of the “dumbbells” are found in the center of the oxygen bi-octahedra¹. These bi-octahedra are linked through corner-sharing Sb-centered octahedra (see Fig. 1). The Cu-Sb “dumbbells” have equal probability to have “up” or “down” position¹ and order antiferroelectrically on a short scale to compensate for the strong dipole moment of the nearest neighbor “dumbbells”. This arrangement results in nanoscale honeycomb Cu^{2+} fragments which are of high theoretical interest^{8,9}.

In $\text{Ba}_3\text{CuSb}_2\text{O}_9$ orbital and magnetic degrees of freedom arise from Cu^{2+} . In general, the Cu^{2+} environment tends to experience Jahn-Teller (JT) distortion which removes the degeneracy of electronic orbitals and distorts oxygen octahedra. This effect has a simple description only in a lattice containing only Cu^{2+} atoms at the rel-

evant positions. When Cu^{2+} are introduced into a host lattice, a competition between JT distortion and a resulting strain of the host lattice defines the size, direction and dynamic or static nature of the JT distortion of Cu^{2+} environment^{11,12}. The $\text{Ba}_3\text{CuSb}_2\text{O}_9$ structure, where the Cu^{2+} -centered oxygen octahedra share a face with JT-inactive Sb-centered octahedra leads to a decrease of the JT energy⁵. To have properties of a spin-orbital liquid $\text{Ba}_3\text{CuSb}_2\text{O}_9$ structure should be free of static JT distortion^{1,10}.

The interest in this system originates from the fact that for “hexagonal” samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ no collective JT distortion is observed, and the overall hexagonal $P6_3/mmc$ symmetry is preserved^{1,2}. For this phase, no magnetic phase transition or spin glass freezing is found down to the lowest accessed temperatures^{1,3}. The disorder in the Cu-Sb positions prevents X-ray techniques from reliably detecting a presence or absence of JT distortion. The basic question about the presence of locally disordered or dynamic JT distortion in this material is to be answered.

In the “orthorhombic” samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ which apparently are obtained by a small change in Sb:Cu ratio¹ a transition into orthorhombic low temperature structure below 190 K associated with collective JT distortion is observed, as well as spin freezing at 110 mK. From the temperature of the transition the characteristic energy scale of orbital interactions is estimated to be on the order of 190 K, while superexchange interactions between nearest Cu^{2+} are of the order of 50 K, as deduced from the analysis of inelastic powder neutron scattering. In the “hexagonal” sample, if the JT distortion is dynamic or absent, these two energy scales can mix, resulting in a spin-orbital liquid state¹.

We present a comparative study of single microcrystals of the “hexagonal” and “orthorhombic” $\text{Ba}_3\text{CuSb}_2\text{O}_9$ by Raman scattering spectroscopy. Raman scattering has an

advantage in studies of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ because it produces results both for ordered and disordered phases being sensitive to both collective and local excitations. Structural phase transitions can be observed in Raman scattering through the change of symmetry, number, and polarization of the phonon modes, while local symmetry breaking results in a relieve of degeneracy of local vibrational modes. Raman spectroscopy is a particularly good tool to study JT distortion in various perovskite materials¹³. In Ref. 2 we presented a part of our results on Raman scattering of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ which confirm the persistence of average hexagonal symmetry of the “hexagonal” sample down to low temperatures. Here we present a detailed report on our results. We demonstrate the importance of disorder for the properties of $\text{Ba}_3\text{CuSb}_2\text{O}_9$, present clear evidence of orthorhombic and hexagonal low temperature phases, and discuss the JT distortion observed to a different extend in both compounds.

II. EXPERIMENTAL

Microcrystals of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ were synthesized according to Ref. 1. As was shown in Ref. 1, the samples of “hexagonal” phase have 2:1 ratio of Sb:Cu, while “orthorhombic” samples show a deviation from this stoichiometry, typically with the increase of Sb concentration.

Raman scattering was measured for single microcrystals which had a shape of platelets with the most developed face corresponding to the (ab) plane, that was less than $0.5 \times 0.5 \text{ nm}^2$ size. The measurements were performed with a Horiba Jobin-Yvone T64000 spectrometer equipped with an Olympus microscope, using the 514.5 nm line of the Spectra-Physics $\text{Ar}^+ \text{-Kr}^+$ laser for excitation. The laser power on the sample was kept below 1mW, the temperature of the sample was estimated by comparing Stokes and anti-Stokes parts of the spectra. Low temperature spectra were measured using a Janis ST-500 microcryostat. The samples were fixed on the cold finger using silver paint.

The measurements were performed in the backscattering geometry with vectors of electrical field of excitation light e_L and scattered light e_S lying in the (ab) plane. Data were acquired for two polarizations, ($x'x'$) polarization was measured with $e_L \parallel e_S$, and ($x'y'$) with $e_L \perp e_S$. Due to the very small crystal size, e_L was oriented at a random angle θ to the unit cell axis a in the (ab) plane. We observe Raman scattering proportional to components of plarizability α_{xx} , α_{yy} , and α_{xy} in both of measured polarizations (see Eq. 1).

$$\begin{aligned} I_{(x'x')} &\sim (\alpha_{xx}\cos^2\theta + \alpha_{yy}\sin^2\theta + \alpha_{xy}\sin 2\theta)^2 \\ I_{(x'y')} &\sim (\alpha_{xy}\cos 2\theta + 1/2(\alpha_{yy} - \alpha_{xx})\sin 2\theta)^2 \end{aligned} \quad (1)$$

The dependence of intensity of the Raman spectra on polarization allows us to distinguish between different

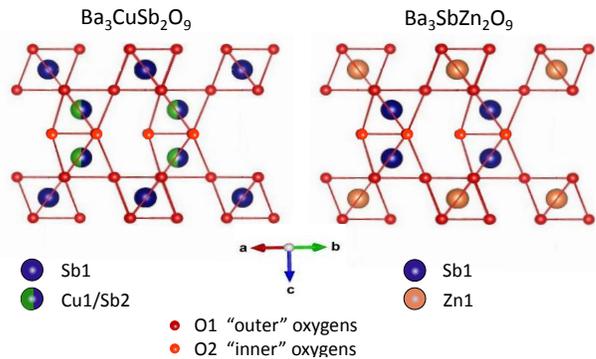


FIG. 1. A scheme of the oxygen octahedra structure of the studied compounds. Left panel : Room temperature hexagonal $P6_3/mmc$ structure of $\text{Ba}_3\text{CuSb}_2\text{O}_9$. Right panel : hexagonal $P6_3/mmc$ structure of $\text{Ba}_3\text{ZnSb}_2\text{O}_9$.

components of polarizability and vibrations of different symmetries.

III. RESULTS

A. Room temperature

Following the crystal structure, the factor group analysis assumes crystallographically equal centers (Sb2, Cu1) for the bioctahedra of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ which yields average hexagonal $P6_3/mmc$ structure. It produces 19 Raman active vibrations: $5A_{1g} + 6E_{1g} + 8E_{2g}$ see Table I for details. According to polarizability tensors for $P6_3/mmc$ space group shown below, in the Raman spectra measured in the (ab) plane we observe modes of A_{1g} and E_{2g} symmetries.

$$\begin{aligned} A_{1g} &= \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} & E_{2g} &= \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ E_{2g} &= \begin{pmatrix} 0 & -d & 0 \\ -d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

At room temperature we compare Raman spectra of both samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ with a powder sample of $\text{Ba}_3\text{ZnSb}_2\text{O}_9$ (Fig. 2). We expect $\text{Ba}_3\text{ZnSb}_2\text{O}_9$ to show phonon spectra similar to $\text{Ba}_3\text{CuSb}_2\text{O}_9$ in $P6_3/mmc$ phase due to similarities of the crystal structures. The $\text{Ba}_3\text{ZnSb}_2\text{O}_9$ structure consists of oxygen bioctahedra with centers occupied by Sb, connected by the corner-sharing oxygen octahedra which have Zn atom in their centers (Fig. 1). This structure can not have JT distortion and does not contain disorder. In $\text{Ba}_3\text{CuSb}_2\text{O}_9$ the centers of all corner-shared oxygen octahedra are occupied by Sb1, and thus preserve translational symmetry, while the centers of double-octahedra contain the randomly up- or down- oriented Cu1-Sb2 “dumbbells”.

In both structures oxygens occupy two crystallographically different sites. O1 are located at the corners of

TABLE I. Site symmetry and irreducible representations for hexagonal $P6_3/mmc$ structure of $Ba_3CuSb_2O_9$.

Atom	Wyckoff position	Cite symmetry	Irreducible Representation
Ba1	2b	-6m2	E_{2g}
Ba2	4f	3m.	$A_{1g}+E_{1g}+E_{2g}$
Sb1 (Zn)	2a	-3m.	not Raman active
Sb2, Cu1 (Sb)	4f	3m.	$A_{1g}+E_{1g}+E_{2g}$
O1 outer	12k	.m.	$2A_{1g}+3E_{1g}+3E_{2g}$
O2 inner	6h	mm2	$A_{1g}+E_{1g}+2E_{2g}$

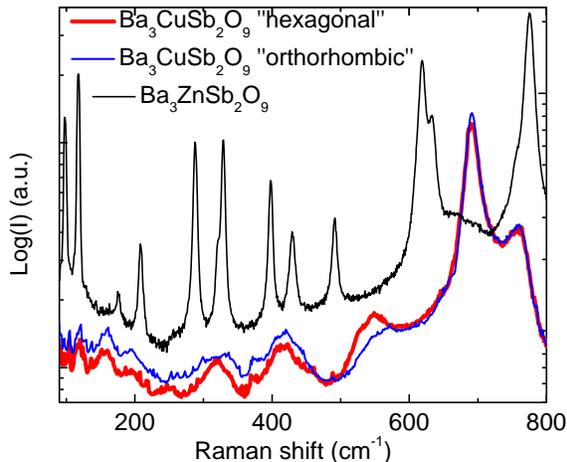


FIG. 2. A comparison of the room temperature ($x'x'$) spectra of $Ba_3CuSb_2O_9$ (red line) and $Ba_3ZnSb_2O_9$ powder sample (black line). Note the much larger width of $Ba_3CuSb_2O_9$ phonon bands due to structural disorder in this compound.

the corner-sharing octahedra (“outer oxygens”), and O2 are found at the shared face of the bioctahedra (“inner oxygens”). The Cu1-Sb2 dumbbells lower the local symmetry for O2 “inner oxygen” sites from C_{2v} to C_2 . The C_2 symmetry of O2 “inner oxygen” sites yields $\Gamma_R=A_{1g}+2E_{1g}+2E_{2g}$ Raman active modes, adding one extra E_{1g} mode inactive in (ab) plane (Table I). However, a local JT distortion around Cu atoms relieves degeneracy of both E_{1g} and E_{2g} modes of the involved oxygens, that would influence the measured spectra.

The most striking difference between the spectra of $Ba_3ZnSb_2O_9$ and $Ba_3CuSb_2O_9$ (see Fig. 2) is the line width of the observed phonons. Most of the bands in $Ba_3CuSb_2O_9$ spectra show the width larger than 20 cm^{-1} . The only relatively narrow peaks are found above 600 cm^{-1} . Vibrations of the metal atoms in the range below 200 cm^{-1} (Ref. 14) are extremely widened (see Fig. 2) and are difficult to distinguish from the scattering background. In contrast to that, the Raman spectra of $Ba_3ZnSb_2O_9$ powder sample show well-defined

phonon peaks with the half-width below 10 cm^{-1} . The large line width is an evidence of the strong structural disorder in $Ba_3CuSb_2O_9$ samples. In contrast to an ordered material, where a line width is defined by a lifetime of a level and is typically about few wavenumbers, in a disordered system the k -dependence is lost. The width of the bands observed in the Raman spectrum of $Ba_3CuSb_2O_9$ are defined by the phonon density of states (DOS)¹⁵. An absence of k -dependence suggests that a coherent length of an ordered pattern is less than $1/10$ of the excitation laser line frequency or 50 nm in the current case, which is in agreement with the estimation of the coherent structure on the order of 10 \AA for $Ba_3CuSb_2O_9$ (Ref. 1). The coherent length of the ordered pattern is so small that we cannot distinguish between the coherent hexagonal arrangement of dumbbells suggested in Ref. 1 or stripe-like arrangement proposed in Ref. 10.

Our main aim is to follow JT distortion in $Ba_3CuSb_2O_9$, thus in course of the paper our attention is focused on the stretching oxygen vibrations, found in $700\text{-}500\text{ cm}^{-1}$ frequency range^{13,16}. We use symmetry analysis, and data on the Raman spectra of various transitional metal oxides¹⁴ for their assignment.

According to the Eq (1), since for $P6_3/mmc$ group $\alpha_{xx} = \alpha_{yy} = a$, for any orientation of the crystal the intensity of A_{1g} modes in ($x'y'$) will be equal to zero, while E_{2g} will be observed in both polarizations at any orientation. At room temperature, in the ($x'y'$) spectra of both samples of $Ba_3CuSb_2O_9$ the intensity of A_{1g} modes is reduced but detectable (see Fig. 3). It shows that the disorder associated with the random Cu1/Sb2 positions or local JT distortion of Cu^{2+} leads to violation of the selection rules¹⁵.

Stretching vibrations of “outer oxygens” are found at $760\text{-}690\text{ cm}^{-1}$ range in $Ba_3CuSb_2O_9$ spectra. The SbO_6 octahedra preserve translational symmetry and therefore we expect the O1 modes to have the lowest line width (see Figs. 4, 5). In accord with polarization dependence of the bands at 760 and 690 cm^{-1} (see Fig. 3) we assign them respectively to E_{2g} and breathing A_{1g} modes of SbO_6 corner-sharing octahedra. The frequencies of these vibrations are relatively close to the frequencies of the A_{1g} breathing mode (709 cm^{-1}) and E_{2g} mode (670 cm^{-1}) of the corner-sharing SbO_6 octahedra in Ba_2BiSbO_6 ¹⁷. The same vibrations of O1 in corner sharing Zn-centered octahedra of $Ba_3ZnSb_2O_9$ are found at higher frequencies, with A_{1g} mode at 776 cm^{-1} , and E_{2g} mode showing up as a weak shoulder at 755 cm^{-1} . Interestingly, in contrast to many other perovskites¹³, in $Ba_3CuSb_2O_9$ the E_{2g} mode is relatively intense and shows higher frequency than the A_{1g} mode.

A number of wide overlapping bands is observed in $500\text{-}650\text{ cm}^{-1}$ range, where we expect stretching vibrations of the “inner” oxygens O2^{14,18,19} which have larger line width. In spectra of ($x'x'$) polarization below 200 K (Fig. 3) we find 645 cm^{-1} band assigned to the A_{1g} breathing mode of the O2 shared-face of the double-octahedra.

TABLE II. Frequencies of the stretching vibrations and their assignment.

Ba ₃ ZnSb ₂ O ₉ at RT (cm ⁻¹)	“Hexagonal” at RT (cm ⁻¹)	“Orthorhombic” at RT (cm ⁻¹)	Polarization at RT	Symmetry at RT	“Orthorhombic” at 15 K	Assignment
755	760	760	(<i>x'x'</i>), (<i>x'y'</i>)	E _{2g}	771 (<i>x'x'</i>) A _g 752 (<i>x'y'</i>) B _{1g}	O1 Jahn-Teller mode of the SbO ₆ octahedra
776	690	690	(<i>x'x'</i>)	A _{1g}	694 (<i>x'x'</i>) A _g	O1 breathing of SbO ₆ octahedra
	645 LT		(<i>x'x'</i>)	A _{1g}	645 (<i>x'x'</i>) A _g	breathing of O2
631	567 w in (<i>x'x'</i>)	570	(<i>x'x'</i>), (<i>x'y'</i>)	E _{2g}	589 (<i>x'x'</i>) A _g 568 (<i>x'x'</i>), (<i>x'y'</i>) B _{1g}	O2 stretch “orthorhombic” sample O2 stretch “orthorhombic” sample
618	550	545	(<i>x'x'</i>), (<i>x'y'</i>)	E _{2g}	547 (<i>x'x'</i>), (<i>x'y'</i>) A _g , B _{1g}	O2 stretch
	526		(<i>x'x'</i>)	E _{2g}		O2 stretch “hexagonal” sample

The two E_{2g} bands of O2 oxygens are found at 570 and 547 cm⁻¹ for the “orthorhombic” sample. In the “hexagonal” sample we observe the 567 cm⁻¹ band mostly in (*x'y'*) and a lower-lying band at 526 cm⁻¹ in (*x'x'*). This considerable difference in frequencies of E_{2g} bands indicates differences in the details of the structure of double-shared octahedra between “hexagonal” and “orthorhombic” samples already at room temperature. These findings are consistent with the single crystal x-ray diffraction studies² which show that Cu1-Sb2 “dumbbells” are slightly elongated and shifted in the *z* direction in the structure of “hexagonal” samples in such a way that Sb atom is found close to “inner” oxygens, and Cu atoms is found farther away from them.

Bands at 410 and 310 cm⁻¹ arise from tilting and bending modes of the oxygen octahedra^{13,14}. These frequencies are less dependent on the type of the metal ion in the center of the octahedra. Indeed, we observe them at similar frequencies for Ba₃CuSb₂O₉ and Ba₃ZnSb₂O₉ with a much larger bandwidth in the spectra of Ba₃CuSb₂O₉.

Main results of room temperature measurements (i) We observe high level of disorder in both samples of Ba₃CuSb₂O₉; the disorder affects the vibrations of the “inner” oxygens more than that of the “outer” oxygens. While the presence of Sb2-Cu1 dumbbells itself introduces the disorder, the major effect on the oxygen vibrations suggests that the disordered JT distortion of Cu²⁺ environment is present at room temperature; (ii) We observe differences in spectra of “orthorhombic” and “hexagonal” samples in the region of stretching “inner” oxygen vibrations consistent with the differences in the position of Cu-Sb dumbbells detected by X-ray scattering.

B. Cooperative JT distortion in the “orthorhombic” sample below 200 K

According to x-ray diffraction and EXAFS data¹, upon cooling down below approximately 190 K the “orthorhombic” sample undergoes a structural phase transition from *P6₃/mmc* to *Cmcm* symmetry accompanied by a doubling of the unit cell along *b* axis. The transition is broad, as expected from a disordered system, and is characterized by a co-operative JT distortion of oxygen octahedra driven by six-fold coordinated Cu²⁺.

While the JT transition impacts the Cu²⁺ environment most directly, it also leads to a distortion of the SbO₆ corner-shared octahedra. In case of incoherent JT distortion only those “outer” oxygens which share a corner with a Cu²⁺-centered octahedra will shift from the higher-symmetry *m*. positions. In the orthorhombic *Cmcm* structure with collective JT distortion all SbO₆ octahedra lose C₃ symmetry axis¹. Thus the relatively narrow oxygen vibrations of the SbO₆ corner-shared octahedra can be a sensitive probe of the JT distortion of Cu²⁺ environment. If the disordered JT distortion is present in the high-temperature phase, the structural transition associated with collective JT distortion will show features of an ordering transition²⁰.

The factor group analysis for oxygen modes in *Cmcm* can be found in Table III, and the polarizability tensors relevant to our measurements in the (ab) plane are presented below:

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, B_{1g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

A JT distortion is expected to lift the degeneracy of doubly degenerate vibrations, so that in the (ab) plane

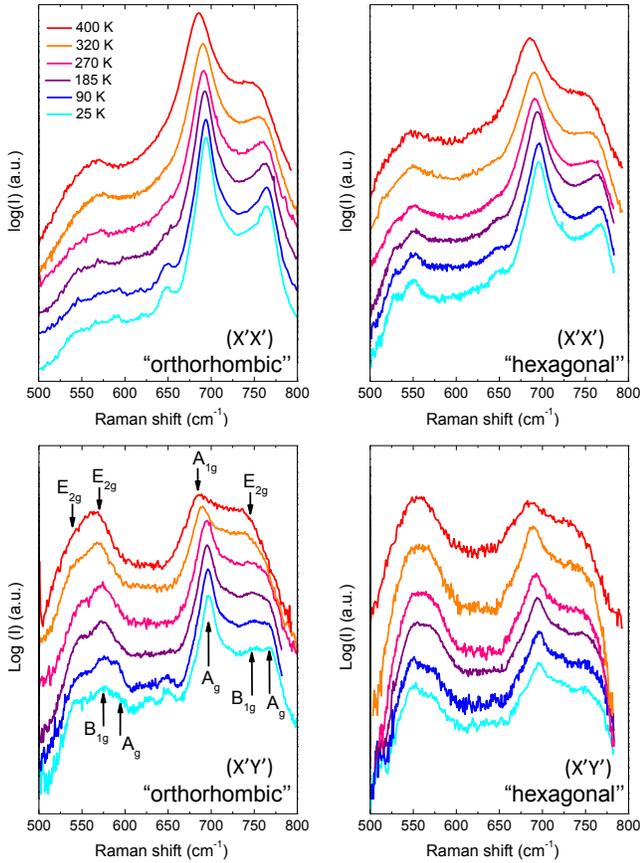


FIG. 3. Temperature dependence of the Raman spectra of the “orthorhombic” and “hexagonal” samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$. Left panels show $(x'x')$ (upper) and $(x'y')$ (lower) for the “orthorhombic” sample. The symmetry of the stretching oxygen vibrations discussed in the text is marked for $(x'y')$ polarization in hexagonal $P6_3/mmc$ and orthorhombic $Cmcm$ phases. Right panels show $(x'x')$ (upper) and $(x'y')$ (lower) for the “hexagonal” sample which shows no changes on cooling.

TABLE III. Site symmetry and irreducible representations for oxygen vibrations for the orthorhombic $Cmcm$ structure of $\text{Ba}_3\text{CuSb}_2\text{O}_9$.

Atom	Wyckoff position	Cite symmetry	Irreducible Representation
O1 ‘inner’	8g	m	$2A_g + 2B_{1g} + B_{2g} + B_{3g}$
O2 ‘outer’	8f	mm2	$2A_g + B_{1g} + B_{2g} + 2B_{3g}$
O3 ‘outer’	16h	1	$3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}$
O4 ‘inner’	4c	m2m	$A_g + B_{1g} + B_{3g}$

we will observe $E_{2g} \rightarrow A_g + B_{1g}$, where A_g vibrations give contribution to α_{xx} polarization, and B_{1g} vibrations contribute to α_{xy} . Indeed, new phonon bands appear at temperatures below 200 K in the spectra of the “orthorhombic” sample (see Fig. 3 and Table II), evidencing for this structural change.

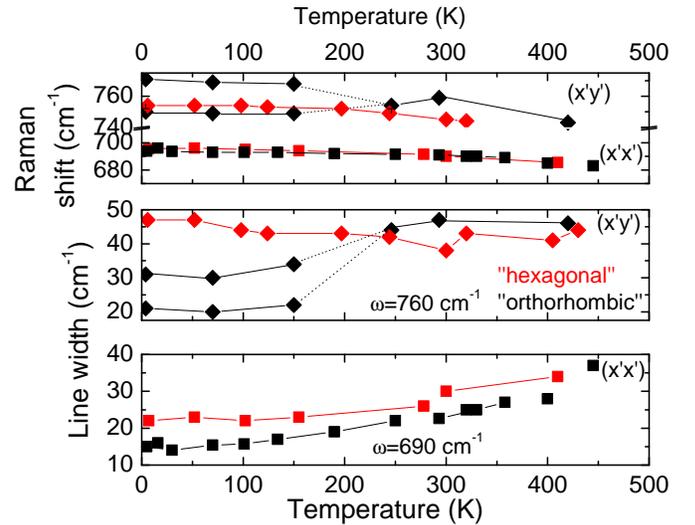


FIG. 4. Temperature dependence of the frequencies and line width of the vibrations of the oxygens of SbO_9 octahedra (“outer oxygens”) for “hexagonal” (red curves) and “orthorhombic” (black curves) samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$. Breathing vibration at 690 cm^{-1} is distinctly observed in $(x'x')$, while the splitting of E_{2g} mode at about 760 cm^{-1} for the “orthorhombic” sample is well-detected in $(x'y')$ polarization. Note a decrease of the the line width for both vibrations for the “orthorhombic” compound in the temperature range of 100-200 K, associated with an appearance of collective JT distortion.

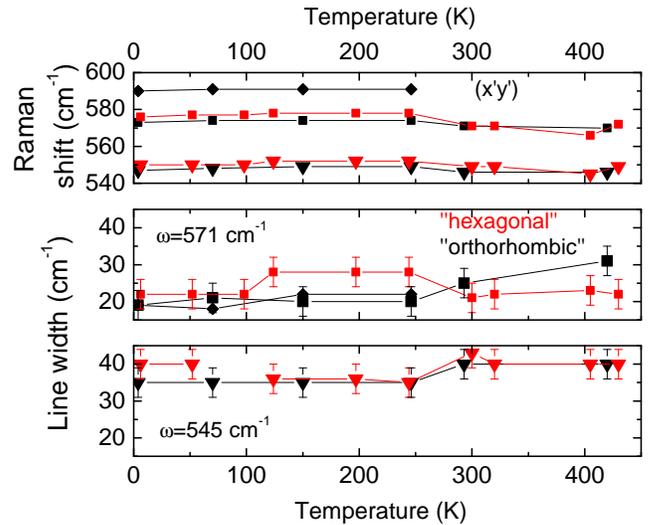


FIG. 5. Temperature dependence of the frequencies and line width of the vibrations of the oxygens of the shared face of the CuSbO_9 octahedra (“inner oxygens”) in $(x'y')$ polarization for “hexagonal” (red curves) and “orthorhombic” (black curves) samples of $\text{Ba}_3\text{CuSb}_2\text{O}_9$. Note large band width not dependent on temperature, which reveals the influence of disorder.

As a result of a transition to $Cmcm$ structure, the E_{2g} (760 cm^{-1}) band of SbO_6 octahedra splits into A_g band at 771 cm^{-1} and a B_{1g} band at 752 cm^{-1} (see Figs. 3,4 and Table II). In addition, we observe an increase in intensity of the A_g vibrations of “outer” oxygens at 695 cm^{-1} and “inner” oxygens at 645 cm^{-1} in the $(x'y')$ spectra in the “orthorhombic” phase. As follows from Eq. 1 for $(x'y')$ polarization in orthorhombic symmetry where $\alpha_{xx} = a \neq \alpha_{yy} = b$, A_g modes would show finite intensity if e_L and e_S are not parallel to the unit cell axis. The line width of these bands associated with “outer” oxygens continuously decreases on cooling (Fig. 4), suggesting that life-time broadening is larger than that due to disorder.

The temperature dependent changes for E_{2g} modes of “inner oxygens” are more difficult to detect, since the bands are wide and overlapping. The E_{2g} mode at 570 cm^{-1} splits into A_g at 589 cm^{-1} and a B_{1g} at 568 cm^{-1} . We do not see a distinct splitting of the second E_{2g} mode at 545 cm^{-1} . The line widths of these vibrations are temperature independent and remain larger than 20 cm^{-1} , which indicates the line widths are defined by disorder (Fig 5).

C. Absence of cooperative JT distortion in the “hexagonal” sample

Upon cooling no new phonon bands appear in the spectra of the “hexagonal” sample, confirming that the average hexagonal symmetry is preserved. The frequencies of vibrational bands harden similar to the “orthorhombic” sample, while the line widths of the bands remain large or increase on cooling.

The E_{2g} (760 cm^{-1}) band of SbO_6 octahedra does not show a distinct splitting of the orthorhombic phase. However, the width of this band increases on cooling (Fig. 4(b)). This behaviour is reversed to the one expected from the life-time broadening. As we discussed in Section III A, the major origin of the line broadening in these compounds is disorder associated with JT distortion of the Cu^{2+} environment, which relieves the degeneracy of doubly degenerate modes. The increase of the line width on cooling indicates the increase of the amplitude of the JT distortion.

The A_g vibrations of the “outer” oxygens at 695 cm^{-1} mode keep constant intensity relative to E_{2g} in $(x'y')$ polarization on cooling, in contrast to the “orthorhombic” sample, suggesting that the symmetry of the unit cell is preserved. Below 200 K the line width for the “hexagonal” sample stays independent of temperature, evidencing for the persistent structural disorder (see Fig. 4(c)).

Main results for temperature dependence (i)

The temperature dependence of the Raman spectra of the “orthorhombic” sample is consistent with a change of symmetry from $P6_3/mmc$ to $Cmcm$ below about 190 K associated with a collective JT distortion of Cu^{2+} environment. Below the transition the signatures of the disorder

for “outer” oxygen vibration decreases. (ii) The temperature behavior of the Raman spectra of the “hexagonal” sample confirms that $P6_3/mmc$ space group describes the average structure in the whole measured temperature range. The increase of the width of the band of “outer” oxygen at 760 cm^{-1} on temperature decrease suggests an increase of the amplitude of the local JT distortion in the “hexagonal” sample.

IV. DISCUSSION

Our Raman results are an important evidence of the preserved average hexagonal symmetry for the “hexagonal” sample down to low temperatures. It is an essential point for a possible realization of spin-orbital liquid in this compound.

In the “hexagonal” sample, as well as in the “orthorhombic” sample at high temperatures Raman scattering provides evidence of local disorder caused by JT distortion of the Cu^{2+} environment. In the “hexagonal” sample the effects due to JT distortion increase on cooling while staying local and disordered, and smaller in amplitude than in the “orthorhombic” sample.

There are two possible interpretations of the observed disordered JT distortion in the “hexagonal” sample (i) disordered static (ii) dynamic. If JT distortion is static, the shorter “outer”-O-Cu bonds in the room temperature structure of the “hexagonal” sample compared to that of the “orthorhombic” sample can lead to larger values of superexchange interaction J_1 in it². The increase of the amplitude of the local JT distortion in the “hexagonal” sample on cooling can lead to an additional change of J_1 .

If JT distortion is dynamic, but its frequency is at least an order of magnitude lower than the used probe, it would affect the line shapes of the relevant phonons in the same way as a static distortion²¹. The frequencies of these phonons are about 500 cm^{-1} which puts a high-frequency limit on the frequency of the dynamic JT distortion non-distinguishable from static one of ν_{JT} of 1.5 THz . The recent work on ESR⁵ suggests dynamic JT distortion in the “hexagonal” sample with ν_{JT} fluctuation frequency between 50 GHz at 100 K and about 10 GHz at 20 K , which would be observed as static JT distortion in Raman scattering. Dynamic JT distortion would enable the spin liquid scenario proposed in Ref. 10, which suggest a state where spin singlets are dynamic due to a hopping of orphan spins around the ordered clusters on the lattice.

V. CONCLUSION

We performed a Raman scattering study of “orthorhombic” and “hexagonal” samples of single crystals of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ in a temperature range from 400 to 20 K . We show that the shape of the Raman phonon spectra are defined by high structural disorder observed in

$\text{Ba}_3\text{CuSb}_2\text{O}_9$, with the coherent length of ordered patterns less than 50 nm.

We follow the crystallographic phase- and temperature dependence of the oxygen stretching vibrations, which show the highest sensitivity to JT distortion of Cu^{2+} environment. Our results suggest that “orthorhombic” and “hexagonal” samples possess small differences in the structure of CuSbO_9 biotahedra at temperatures above the structural transition.

For the “orthorhombic” sample our results are in agreement with a transition from hexagonal $P6_3/mmc$ to orthorhombic $Cmcm$ structure due to co-operative JT distortion below 200 K. This structural change is observed as a splitting of doubly-degenerate phonons and a change of polarization dependence of A_g phonons. Analysis of the line width of vibrations of the corner-sharing SbO_6 octahedra suggests that the hexagonal to orthorhombic

crossover has an order-disorder character.

We demonstrate that “hexagonal” sample of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ preserves the average hexagonal symmetry down to 20 K. The analysis of line width of oxygen phonons suggest local JT distortion of Cu^{2+} environment. The distortion amplitude increases on cooling while always staying smaller than the distortion in the “orthorhombic” sample. This disordered local JT distortion in the “hexagonal” sample is either static or dynamic with frequency ν_{JT} lower than 1.5 THz.

VI. ACKNOWLEDGEMENTS

The work at IQM was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences and Engineering under Grant No. DE-FG02-08ER46544.

-
- * Corresponding author: drichko@jhu.edu
- ¹ S. Nakatsuji, K. Kuga, K. Kimura, R. Satake, N. Katayama, E. Nishibori, H. Sawa, R. Ishii, M. Hagiwara, F. Bridges, T. U. Ito, W. Higemoto, Y. Karaki, M. Halim, A. A. Nugroho, J. A. Rodriguez-Rivera, M. A. Green, and C. Broholm, *Science* **336**, 559 (2012), <http://www.sciencemag.org/content/336/6081/559.full.pdf>.
 - ² N. Katayama, K. Kimura, Y. Han, J. Nasu, N. Drichko, Y. Nakanishi, M. Halim, Y. Ishiguro, R. Satake, E. Nishibori, M. Yoshizawa, T. Nakano, Y. Nozue, Y. Wakabayashi, S. Ishihara, M. Hagiwara, H. Sawa, and S. Nakatsuji, *Proceedings of the National Academy of Sciences* (2015), 10.1073/pnas.1508941112.
 - ³ J. A. Quilliam, F. Bert, E. Kermarrec, C. Payen, C. Guillot-Deudon, P. Bonville, C. Baines, H. Luetkens, and P. Mendels, *Phys. Rev. Lett.* **109**, 117203 (2012).
 - ⁴ Y. Ishiguro, K. Kimura, S. Nakatsuji, S. Tsutsui, A. Q. Baron, T. Kimura, and Y. Wakabayashi, *Nature communications* **4** (2013).
 - ⁵ Y. Han, M. Hagiwara, T. Nakano, Y. Nozue, K. Kimura, M. Halim, and S. Nakatsuji, *Phys. Rev. B* **92**, 180410 (2015).
 - ⁶ J. Nasu and S. Ishihara, *Phys. Rev. B* **88**, 094408 (2013).
 - ⁷ K. V. Shanavas, Z. S. Popović, and S. Satpathy, *Phys. Rev. B* **89**, 085130 (2014).
 - ⁸ P. Corboz, M. Lajkó, A. M. Läuchli, K. Penc, and F. Mila, *Phys. Rev. X* **2**, 041013 (2012).
 - ⁹ A. Smerald and F. Mila, *Phys. Rev. B* **90**, 094422 (2014).
 - ¹⁰ A. Smerald and F. Mila, *Phys. Rev. Lett.* **115**, 147202 (2015).
 - ¹¹ D. Reinen and S. Krause, *Inorganic Chemistry* **20**, 2750 (1981), <http://dx.doi.org/10.1021/ic50223a002>.
 - ¹² B. Ramakrishna, D. Reinen, and M. Atanasov, *Journal of Solid State Chemistry* **129**, 117 (1997).
 - ¹³ M. N. Iliev and M. V. Abrashev, *Journal of Raman Spectroscopy* **32**, 805 (2001).
 - ¹⁴ U. Treiber and S. Kemmler-Sack, *Zeitschrift für anorganische und allgemeine Chemie* **487**, 161 (1982).
 - ¹⁵ R. Shuker and R. W. Gammon, *Phys. Rev. Lett.* **25**, 222 (1970).
 - ¹⁶ A. P. Ayala, I. Guedes, E. N. Silva, M. S. Augsburger, M. del C. Viola, and J. C. Pedregosa, *Journal of Applied Physics* **101**, 123511 (2007), <http://dx.doi.org/10.1063/1.2745088>.
 - ¹⁷ M. Castro, E. Carvalho, W. Paraguassu, A. Ayala, F. Snyder, M. Lufaso, and C. Paschoal, *Journal of Raman Spectroscopy* **40**, 1205 (2009).
 - ¹⁸ A. Sacchetti, M. Baldini, P. Postorino, C. Martin, and A. Maignan, *Journal of Raman Spectroscopy* **37**, 591 (2006).
 - ¹⁹ Y. S. Lee, T. W. Noh, J. H. Park, K.-B. Lee, G. Cao, J. E. Crow, M. K. Lee, C. B. Eom, E. J. Oh, and I.-S. Yang, *Phys. Rev. B* **65**, 235113 (2002).
 - ²⁰ E. Granado, J. A. Sanjurjo, C. Rettori, J. Neumeier, and S. Oseroff, *Physical Review B* **62**, 11304 (2000).
 - ²¹ R. Kubo, *Stochastic Processes in Chemical Physics* **15**, 101 (1969).