Low temperature Raman study of the spin ladder compound BiCu$_2$PO$_6$

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Abstract. We have investigated the temperature (40-295K) dependence of the Raman active phonons of BiCu$_2$PO$_6$ single crystals oriented along a- and b-axis. The comparison between the two orientations did not show any remarkable effect along the b-axis (two-leg zigzag spin ladder direction). At low temperatures the modes appear shifted and narrowed. The spectral characteristics of the modes below $\sim$60 K show constant values, indicating strong coupling between the formation of spin-ladder and the crystal lattice.

1. Introduction

In recent years quantum antiferromagnets with an intrinsically disordered (“spin liquid”) ground state and an energy gap in the spin excitation spectrum have received a great deal of attentions [1]. In search for new experimental realizations of spin-ladder and related models, we have embarked upon a new interesting family of low-dimensional materials with the general formula BiCu$_2$AO$_6$ ($A = P$, V and As). Among them, BiCu$_2$PO$_6$ (BCPO) shows a structure where Cu$^{2+}$ (S=1/2) spins appear to form two-leg zigzag ladders, which is a valuable model of quantum magnets. For studies including neutron scattering and accurate thermodynamics well characterized large single crystals are indispensable. Detailed studies on the growth of single crystals, and x-ray or neutron powder and Laue diffraction, NMR, and magnetic susceptibility $\chi$(T) measurements were published recently on undoped and Zn-doped samples Bi(Cu$_{1-x}$Zn$_x$)$_2$PO$_6$ (x=1%,5%) [2,3]. It was shown that the magnetic susceptibility $\chi$(T) passes through a broad maximum around 60K confirming the formation of a spin singlet ground state.

In this study, we present the first micro-Raman low temperature spectra of the BiCu$_2$PO$_6$ single crystal. A tentative assignment of the observed bands is suggested based on spectra on single crystals grown of different orientations and from similar compounds. We show that the phonon shift and width narrowing at low temperatures can be associated with the lattice coupling with the low temperature antiferromagnetic state.

2. Experimental

We have studied BiCu$_2$PO$_6$ single crystals (size about $3\times4\times2$mm$^3$, length along each axis) were cut from a boule, grown in an optical furnace by the traveling solvent floating zone method. The crystals were found to be phase pure as confirmed by x-ray powder diffraction [2]. The lattice constants were...
determined as \( a=11.7795\,\text{Å}, \, b=5.1739\,\text{Å}, \, c=7.7918\,\text{Å} \) and space group is \( Pnma \). Concerning the structure, two edge-sharing CuO\(_5\) distorted square pyramids with a Cu\(^{2+}\) ion at the center of the five fold oxygen coordination give rise to a Cu dimer with an intradimer distance of 2.8 Å. Each dimer connects two others by its four O1 corners resulting in a zigzag double chain (ladder) running along the b-axis. The interdimer cohesion is further strengthened by PO\(_4\) tetrahedra that connect two consecutive dimmers by O2 corners. The Bi ions are positioned between two ladders. Sample A indicates that the single crystal is oriented along the a-axis and the spectra are collected from the polished bc surface. Sample B is b-axis oriented with the ac surface polished.

A T64000 Jobin Yvon triple spectrometer was used for the light scattering experiments equipped with a liquid nitrogen cooled charge coupled device and a microscope. The 514.5 nm laser line of an Ar+ laser was used for excitation. The Raman spectra of the single crystals were measured at a temperature region of 40–295 K. A backscattering geometry was used with the sample placed under the microscope with \( \times 100 \) magnification lens. The spectra were recorded without polarization filter for the incident laser and the scattered Raman light. Size and power of the laser spot on the surface was approximately 1 \( \mu \)m and 5 mW. For the low temperature (LT) measurements, an open cycle Oxford cryostat (MicrostatHe) was used. For each single crystal several points of the surface have been studied in order to check their homogeneity, which was confirmed by this surface scanning.

3. Results and Discussion

\[ \begin{align*}
\text{BiCu}_2\text{PO}_6 \quad \text{RT} \\
\text{Intensity (a.u.)} \\
\text{B} \\
\text{BiCu}_2\text{PO}_6 \\
\text{RT} \\
\text{a} \\
\text{c} \\
\text{b} \\
\text{Raman Shift (cm}^{-1}\text{)} \\
200 & 400 & 600 & 800 & 1000 \\
\text{Intensity (a.u.)} \\
\text{A} \\
\text{Figure 1. Typical Raman spectra of the samples a and b in the region 70-1150 cm}^{-1}\text{ measured in random orientation.}
\end{align*} \]

Figure 1 presents the room temperature (RT) Raman spectra obtained by two differently oriented samples, A (B) with incident laser perpendicular to bc (ac) plane. Since samples are differently oriented we can extract information about the selection rules of the observed modes and their Raman tensors. Following the structure analysis, the BCPO contains PO\(_4\) and CuO\(_5\) non magnetic tetrahedra and magnetic square pyramids, respectively. The relative modes are internal for the BCPO compound and therefore are expected at about the same frequencies as in other similar systems [4-12]. The spectra of the \( Td \) symmetry PO\(_4\)\(^{3-}\) ions consist of the \( v_1 \) stretching mode at 938 cm\(^{-1}\) (\( A_1 \)), the doubly degenerate \( v_3 \) bending mode at 420 cm\(^{-1}\) (E), the triply degenerate antisymmetric \( v_1 \) stretching mode at 1017 cm\(^{-1}\) (\( F_2 \)), and the triply degenerate bending mode \( v_3 \) at 567 cm\(^{-1}\) (\( F_2 \)) [4]. All these modes are Raman active, while the last two are IR active as well when there is no inversion symmetry. Reduction
of the symmetry of the \( \text{PO}_4^{3-} \) ion from the \( T_d \) symmetry to \( C_s \) results to a splitting of the \( F_2 \) to the \( 2A_1 \) and \( A_2 \) modes that appear at lower shifted energies in the Raman and IR spectra [4]. In the same way the \( \text{CuO}_3 \) pyramids contribute in the spectra, by bonds attributed to \( \text{Cu-O} \) vibrating bonds. Similar bonds appear in LaSrCuO\(_4\) [5], \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) [6], \( \text{CuO} \) single crystals [7] and \( \text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{CuO}_{4+\delta} \) [8,9] systems. Typical frequencies of vibrations related to the \( \text{Cu-O} \) bonds are at \( \sim 130 \text{cm}^{-1}, \sim 225 \text{cm}^{-1}, \sim 270 \text{cm}^{-1}, 350 \text{cm}^{-1}, 1110 \text{ cm}^{-1} \) and many other reported in similar compounds [8,9].

A detailed analysis of the expected modes, combined with lattice dynamic calculations and additional scattering configuration measurements to provide the exact selection rules and assignment of the modes in this system, will be published elsewhere. In summary, in Figure 1, the modes at 128 cm\(^{-1}\), 209 cm\(^{-1}\), and 276 cm\(^{-1}\) almost coincide in frequency with those of the \( \text{Cu-O} \) vibrations of other compounds [5-7] and should be related with them. Most of the lower intensity frequency modes around 300 cm\(^{-1}\) (Fig.2 and more pronounced in Fig.3) can be attributed to the vibrations of \( \text{Bi}_2\text{O}_3 \) [9] or the \( \text{BiO}_4 \) pyramids [10]. In the \( v_2 \) PO\(_4\) bending mode two distinguishable peaks appear at 405 and 420 cm\(^{-1}\), while in the \( v_4 \) PO\(_4\) bending mode four distinguishable peaks appear at 539, 558, 610, and 630 cm\(^{-1}\) with orientation dependent intensity. In the region of the \( v_3 \) PO\(_4\) stretching mode three peaks exist at 1022 cm\(^{-1}\), 1061 cm\(^{-1}\), and 1090 cm\(^{-1}\) with intensity strongly dependent on orientation. The \( v_1 \) PO\(_4\) stretching mode appears at 962 cm\(^{-1}\), while the bands at 1124 cm\(^{-1}\) and 1139 cm\(^{-1}\) must arise from second order \( \text{Cu-O} \) vibrations [5,11].

**Figure 2.** Low temperature Raman measurements of the BCPO A sample at selected temperatures.

**Figure 3.** Low temperature Raman measurements of the BCPO B sample at selected temperatures.

In the low temperature Raman measurements presented in Fig. 2 and 3 of the two samples at selected temperatures all modes appear, as expected, upshifted and narrower at low temperatures. In addition, all modes gain intensity at low temperatures while some new ones appear or they are better distinguished. In the \( v_2 \) PO\(_4\) region the narrowing at low temperatures give rise to a hidden mode at 397 cm\(^{-1}\), which is better distinguished at the B sample, probably due to orientation effect.
It was shown that the magnetic susceptibility $\chi(T)$ passes through a broad maximum around 60K confirming the formation of a spin singlet ground state [2]. In figure 4, the spectral characteristics of the four modes in the 200 – 420 cm$^{-1}$ region are presented. All phonon characteristics appear to be affected below 80K, while around 60K the formation of a stable spin ground state is indicated by the almost constant values of frequency and width. The 275 cm$^{-1}$ mode appears also strongly asymmetric at low temperatures implying a stronger coupling with the magnetic carriers.

**Figure 4.** The spectral features of the 213, 278, 364 and 408 cm$^{-1}$ phonons for the sample A. Squares mark the phonon frequency, triangles the phonon width and the rhombus the phonon intensity.

### 4. Conclusions

In this work we present the first low temperature Raman spectra of the two-leg spin ladder BiCu$_2$PO$_6$ single crystal. A tentative assignment of the modes is provided. It is found that certain modes attributed to the Cu-O bonds are modified close to the spin gap temperature. This provides a direct evidence of the coupling of the spin ladder formation with the lattice. 

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