Available online at www.sciencedirect.com
SCIENCE DIRECT
Physica B 359–361 (2005) 980–982
PHYSICA B
www.elsevier.com/locate/physb

Crystal structure and lattice dynamics of $SrCu_2(BO_3)_2$ at high pressures

I. Loa[a,*], F.X. Zhang[a], K. Syassen[a], P. Lemmens[a], W. Crichton[b], H. Kageyama[c], Y. Ueda[d]

[a] *Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany*
[b] *European Synchrotron Radiation Facility, F-38043 Grenoble, France*
[c] *Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan*
[d] *Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan*

Abstract

We investigate the effect of hydrostatic pressure on the structural and lattice dynamical properties of $SrCu_2(BO_3)_2$ by angle-dispersive synchrotron X-ray powder diffraction and Raman spectroscopy. $SrCu_2(BO_3)_2$ undergoes a subtle tetragonal-to-monoclinic structural distortion near 5 GPa and a first-order structural transition at 15 GPa. The effects of the structural changes on the magnetic properties of this quasi-two-dimensional quantum antiferromagnet are briefly discussed.

PACS: 61.50.Ks; 62.50.+p; 78.30.Hv; 61.10.Nz

Keywords: $SrCu_2(BO_3)_2$; High pressure; Structural phase transition

$SrCu_2(BO_3)_2$ is a model system of a *frustrated two-dimensional quantum antiferromagnet* and a realisation of the Shastry–Sutherland model [1,2]. The compound is characterised by competing nearest and next-nearest neighbour in-plane spin interactions together with a weak coupling between the layers. Various experiments and theoretical investigations have shown that orthogonally coupled spin-dimer singlets (located on Cu dimers) form a singlet ground state which is separated from dispersionless triplet excitations by a spin gap of $\Delta = 34\,K$ [2–4].

Application of high pressures is the means of choice to change continuously the magnetic coupling constants via the variation of bond lengths. Recent magnetic susceptibility measurements indicate a reduction of the spin–gap under hydrostatic pressures up to 0.7 GPa [5]. On the

*Corresponding author. Tel.: +49 711 689 1469; fax: +49 711 689 1010.
E-mail address: i.loa@fkf.mpg.de (I. Loa).

0921-4526/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2005.01.284

basis of these results, a quantum phase transition has been predicted at a critical pressure of 2.5–3.5 GPa [5].

We investigate here the effect of pressure on the crystal structure and lattice dynamics of $SrCu_2(BO_3)_2$ under hydrostatic pressure. The first purpose of this work is to explore the stability range of the ambient-pressure phase of $SrCu_2(BO_3)_2$ in order to find out whether a pressure-induced quantum phase transition could possibly be intercepted by a structural phase transition. Secondly, we provide high-pressure structural data as a basis for a detailed analysis of the pressure-induced changes in the magnetic properties of $SrCu_2(BO_3)_2$.

The phase stability and lattice dynamical properties of $SrCu_2(BO_3)_2$ were studied by Raman spectroscopy at pressures up to 21 GPa and ambient temperature. The Raman spectra were excited at 633 nm and recorded with a single-stage spectrometer equipped with a holographic notch filter to suppress the laser line (Jobin–Yvon Labram). The structural properties were studied up to 23 GPa and ambient temperature by monochromatic ($\lambda = 0.3738$ Å) X-ray powder diffraction at the European Synchrotron Radiation Facility (ESRF Grenoble, beamline ID30). In both experiments, pressures were generated in diamond anvil high-pressure cells with condensed nitrogen as the pressure transmitting medium. The ruby luminescence method [6] was used for pressure determination. The synthesis of the $SrCu_2(BO_3)_2$ material was described elsewhere [7].

The Raman spectra shown in Fig. 1 evidence two structural transitions at 5–7 and ~15 GPa, respectively. The first transition manifests itself in the disappearance of two low-frequency modes marked A and B and the appearance of two new modes A′ and B′ at slightly lower frequencies. None of the other Raman lines exhibits an anomaly near 6 GPa. The observation that only two out of nine observed Raman modes are affected by the transition indicates the occurrence of a rather subtle structural distortion.

As pressure is increased, the Raman peak C near 300 cm^{-1} decreases in intensity and vanishes completely at ~15 GPa. The Raman spectra undergo radical changes between 14.6 and 16.1 GPa with the number of observed Raman lines increasing from 9 to 20. Clearly, there is a sharp structural phase transition at ~15 GPa which is probably of reconstructive nature. The Raman experiments were complemented by high-pressure infrared absorption measurements at the infrared beamline of the synchrotron ANKA (Karlsruhe). They confirm the subtle distortion near 5 GPa and the abrupt phase transition at 15 GPa.

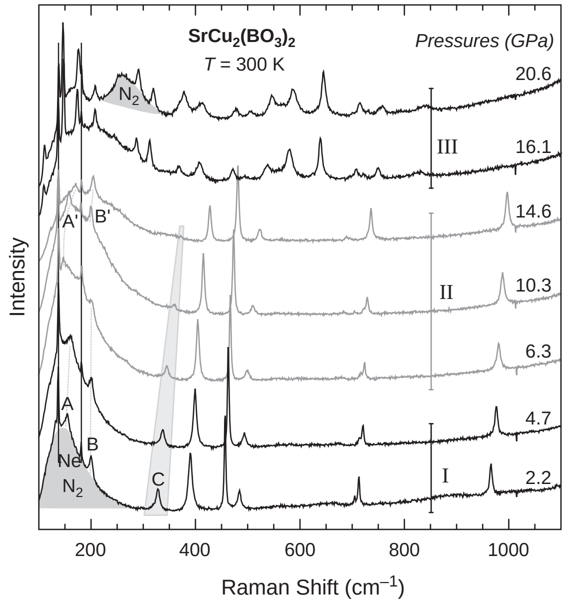

Fig. 1. Raman spectra of $SrCu_2(BO_3)_2$ at pressures up to 21 GPa ($T = 295$ K, $\lambda_{ex} = 633$ nm). The broad band below 200 cm^{-1} originates from the nitrogen pressure medium; the lines marked 'Ne' are neon plasma lines.

X-ray diffraction measurements provide details on the pressure-induced structural changes in $SrCu_2(BO_3)_2$. The diffraction diagrams of phase II between 5 and 15 GPa can be indexed with a monoclinic lattice. The transition near 5 GPa is thus a continuous tetragonal-to-monoclinic distortion (Fig. 2). The structure of the high-pressure phase above 15 GPa remains to be solved. Both structural transitions are fully reversible upon pressure release.

The compressibility of $SrCu_2(BO_3)_2$ is rather anisotropic with the stacking direction c being the soft direction. The anisotropy itself changes with pressure, in particular near the monoclinic

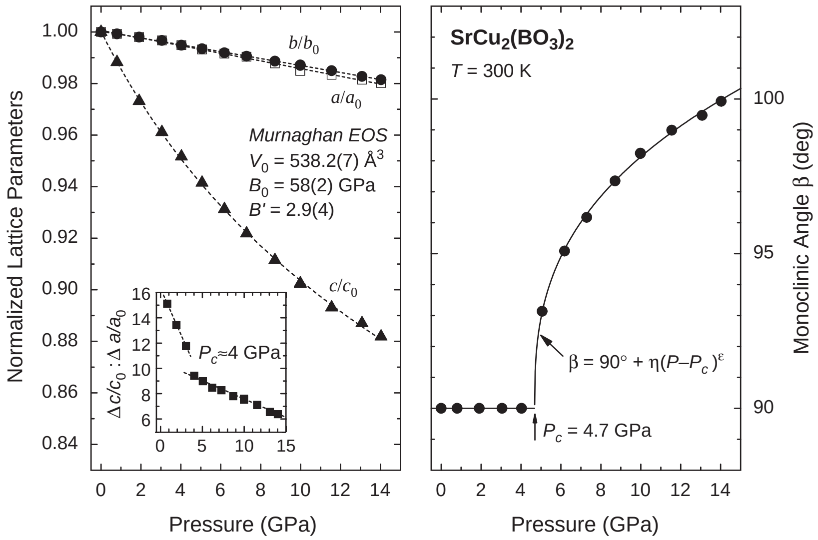

Fig. 2. Normalised lattice parameters of $SrCu_2(BO_3)_2$ as a function of pressure ($a_0, b_0 = 8.9922(3)$ Å, $c_0 = 6.6508(4)$ Å). The inset displays the ratio of the relative compressions $\Delta c/c_0 : \Delta a/a_0$ along c and a.

distortion, as can be seen from the ratio of the relative compressions $\Delta c/c_0 : \Delta a/a_0$ along c and a (inset of Fig. 2). Quite unusually, the axis compressibilities of the a and b axes *increase* with increasing pressures up to ~7 GPa ($B'_a = d^2a/dP^2 < 0$). This can in part be attributed to a reduction of the corrugation of the $Cu_2O_6B_2$-layers under pressure, as a detailed analysis of the diffraction diagrams suggests.

Regarding the magnetic properties of $SrCu_2(BO_3)_2$, the preliminary results presented here let us conclude that it should be possible to reach the quantum critical point at pressures of 2.5–3.5 GPa without the interception of a structural phase transition. The highly anisotropic compression of $SrCu_2(BO_3)_2$ indicates a strengthening of the interlayer magnetic coupling in comparison to the intralayer couplings. A detailed analysis of the intralayer structural changes and their effect on the coupling constants is the subject of ongoing work.

References

[1] B.S. Shastry, B. Sutherland, Phys. Rev. Lett. 47 (1981) 964.
[2] H. Kageyama, K. Yoshimura, R. Stern, N.V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C.P. Slichter, T. Goto, Y. Ueda, Phys. Rev. Lett. 82 (1999) 3168.
[3] S. Miyahara, K. Ueda, Phys. Rev. Lett. 82 (1999) 3701.
[4] A. Koga, N. Kawakami, Phys. Rev. Lett. 84 (2000) 4461.
[5] H. Kageyama, N.V. Mushnikov, M. Yamada, T. Goto, Y. Ueda, Physica B (2003) 329–333.
[6] H.K. Mao, J. Xu, P.M. Bell, J. Geophys. Res. 91 (1986) 4673.
[7] H. Kageyama, K. Onizuka, T. Yamauchi, Y. Ueda, J. Cryst. Growth 206 (1999) 65.