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Magnetic Excitations in PrBa₂Cu₄O₈ Explored by Raman Scattering

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Polarized Raman scattering spectra of PrBa₂Cu₄O₈ were studied in the temperature range 10 to 300 K. An anomalous temperature dependence of the two-magnon peak was found, which softens upon cooling from about 2590 cm⁻¹ at 300 K to 2480 cm⁻¹ at 10 K. The observed behavior is opposite to what is known for RBa₂Cu₃O₆, R₂CuO₄ (R = rare earth) and KMnF₃-type antiferromagnets, where the two-magnon peak shifts to higher frequencies upon decreasing the in-plane Cu–O bond length due to either lowering temperature or applying pressure. The experimental data are discussed in view of the semiconductor–metal transition which, according to recent optical and transport studies, occurs in PrBa₂Cu₄O₈ at $T^* \approx 150$ K.

1. Introduction

The Raman scattering spectroscopy has proven to be an effective method of investigation of high temperature superconductors and related oxides as it allows to yield unique information not only on lattice vibrations, but also on electronic and magnetic excitations, as well as their interactions (for a review, see Refs. [1, 2]). In this paper, we will report the results of an inelastic light scattering study over a broad range of temperatures and scattering energies for PrBa₂Cu₄O₈, a material which attracts attention due to its unique physical properties. It possesses double copper–oxygen chains and is isostructural to the well known RBa₂Cu₄O₈ (R = rare earth) superconductors with critical temperature T_c around 82 K. PrBa₂Cu₄O₈ does not, however, show any signatures of superconductivity down to the lowest temperatures measured. From this point of view it seems instructive to study and compare magnetic excitations for PrBa₂Cu₄O₈ and isostructural superconducting materials. This way one might obtain an insight on the interplay between superconductivity and magnetism, an important old standing question in the field [3].

2. Experimental

The measurements were performed on PrBa₂Cu₄O₈ microcrystallites embedded into a ceramic pellet, which has been prepared by polymerized-complex method at ambient

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pressure [4]. We used a micro-Raman set-up which allowed us to reliably collect polarized spectra from microcrystallites as small as a few micrometers in size. Single- as well as triple-spectrometers, equipped with an optical microscope and liquid nitrogen cooled charge coupled device (CCD) detectors, have been used to collect the scattered light; the spectral resolution was about 12 and 4 cm^{-1} , respectively. We used several lines of an Ar^+ laser with wavelengths in the range 457.9 to 514.5 nm for excitation. For low temperature measurements the sample was mounted on the cold finger of a helium-flow cryostat. The temperature stability was better than 0.5 K.

3. Results and Discussion

The Raman spectra of orthorhombic [5] $\text{PrBa}_2\text{Cu}_4\text{O}_8$ taken at $T = 20$ K in different scattering geometries are shown in Fig. 1. The symmetry of the lattice implies that the scattering components $(x'x')$ and (zz) correspond to A_{1g} symmetry while crossed $(x'y')$ geometry probes B_{1g} symmetry excitations (primed x and y axes are rotated by 45° with respect to the crystallographic a and b axes). The sharp phonon lines in the fre-

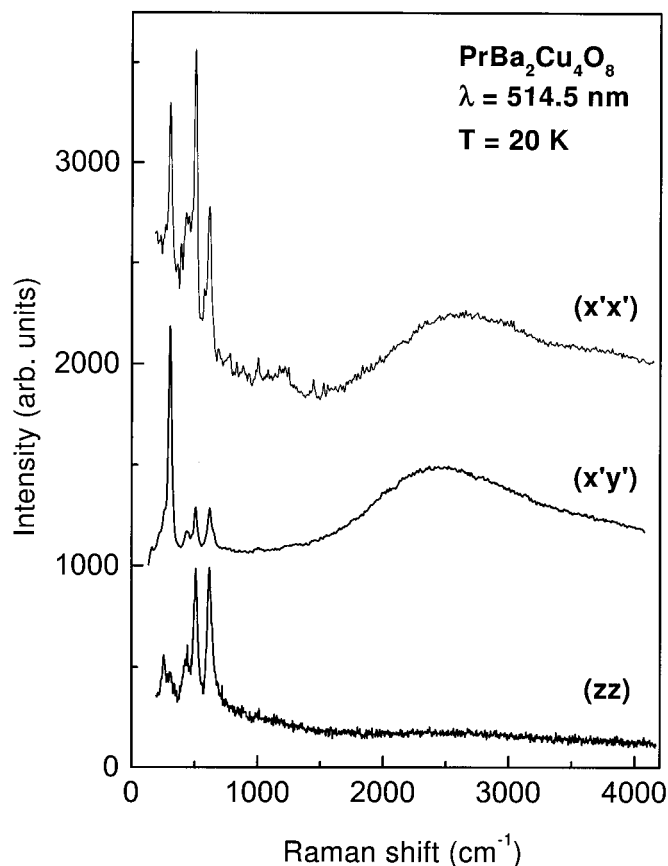


Fig. 1. Polarized Raman scattering spectra of $\text{PrBa}_2\text{Cu}_4\text{O}_8$ at $T = 20$ K. They correspond, from top to the bottom, to A_{1g} , B_{1g} and A_{1g} symmetries, respectively

quency range below 700 cm⁻¹ are due to excitation of even-parity phonons [6]. The line of B_{1g} symmetry at 300 cm⁻¹ dominates the spectrum in (x'y') scattering geometry. The other relatively narrow lines at higher frequencies (510 and 615 cm⁻¹), which represent fully symmetric A_{1g} modes, are most pronounced in the spectra taken with parallel incident and scattered light polarizations.

As is seen from Fig. 1, rather intense broad bands are present in the low temperature scattering spectra of PrBa₂Cu₄O₈ for light polarized within CuO₂ planes (two upper curves in Fig. 1), which are due to the processes of excitation of two zone-edge magnons, like in the case of other antiferromagnetically ordered oxides [2, 7, 8]. Indeed, the Néel ordering temperature of PrBa₂Cu₄O₈ is around 250 K [9] and the peak position (2580 cm⁻¹ at 230 K) is typical for copper oxides [8]. For the ideal tetragonal lattice one expects two-magnon excitations to contribute exclusively to the B_{1g} spectrum under the assumption of nearest-neighbor interactions. It is seen, however, that for orthorhombic PrBa₂Cu₄O₈ the magnon peak intensity is non vanishing also in A_{1g} scattering geometry and the corresponding peak occurs at higher frequency compared to the B_{1g} spectrum. This might be, at least partly, due to contribution to the scattering intensity of

higher order processes [10,11].

It is known that the position of the two-magnon peak (ω_{2M}) is determined by the in-plane exchange energy (J) between two neighboring Cu atoms, and for short-wavelength excitations $\omega_{2M} \approx 2.74 J$ [12], which yields for PrBa₂Cu₄O₈ $J \approx 117$ meV. This value is larger than for single-chain PrBa₂Cu₃O₇ compound (94 meV) [13] and indicates stronger exchange interaction in the double-chain compound.

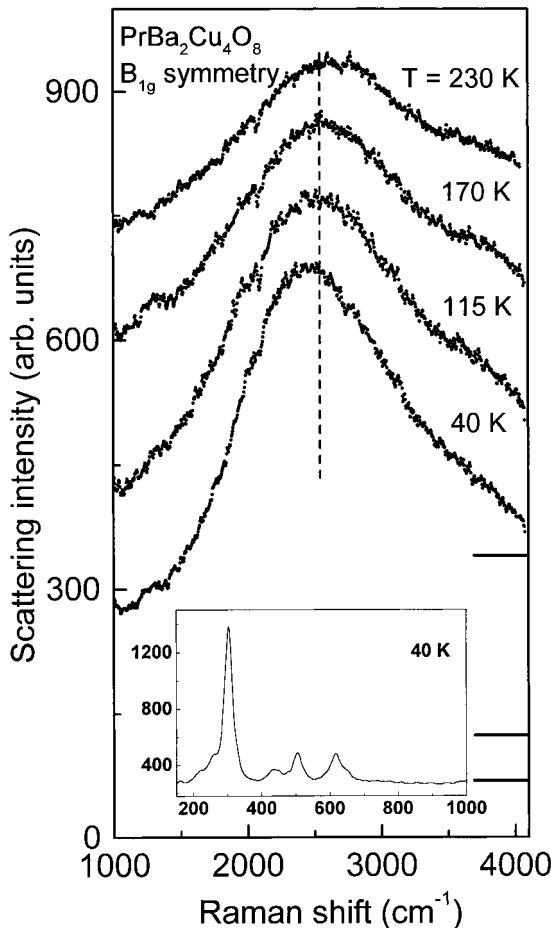


Fig. 2. Two-magnon spectra of PrBa₂Cu₄O₈ in B_{1g} scattering geometry for temperatures between 230 and 40 K. The vertical dashed line marks the peak position at high temperatures. The short solid lines in the right lower corner of the figure denote the baseline position for the three upper spectra. Note the downshift and narrowing of the peak upon sample cooling. The insert shows the low-frequency part of the spectrum which is dominated by the phonon at 300 cm⁻¹

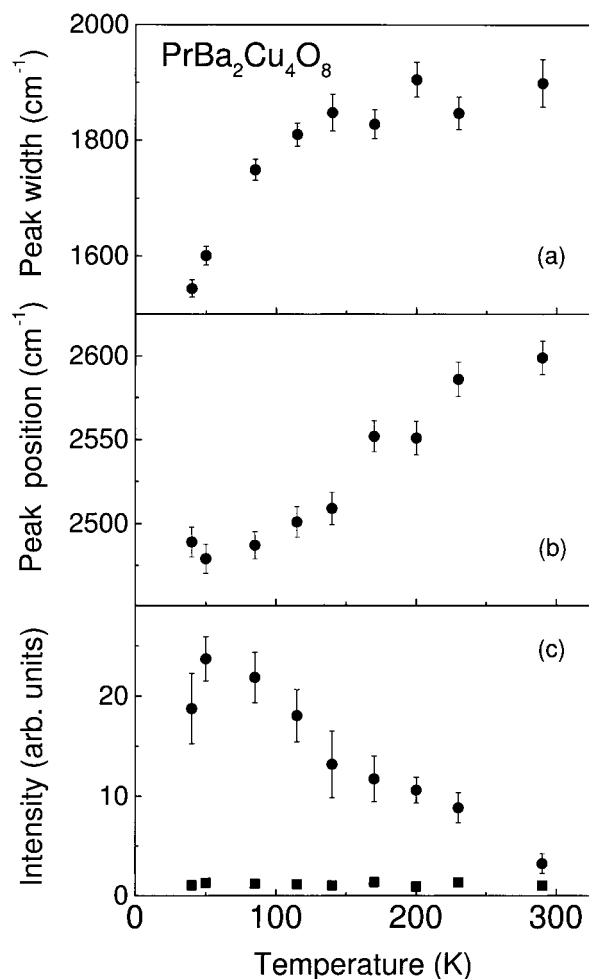


Fig. 3. Temperature dependence of the a) linewidth, b) position, and c) integrated intensity of the two-magnon scattering band of $\text{PrBa}_2\text{Cu}_4\text{O}_8$. The squares in the lower part of c) denote intensity of the B_{1g} phonon at about 300 cm^{-1} .

Raman scattering spectra of $\text{PrBa}_2\text{Cu}_4\text{O}_8$ for various temperatures between 230 and 40 K are shown in Fig. 2 and the results of fits to a single Lorentzian line shape are summarized in Fig. 3.²⁾ As is seen, the two-magnon peak shifts to lower frequencies upon cooling. This is opposite to what is known for, e.g., $\text{RBa}_2\text{Cu}_3\text{O}_6$, R_2CuO_4 and KMnF_3 -type antiferromagnets, where the peak frequency and, correspondingly, J increases upon decreasing the Cu–O bond length either by lowering the temperature [10], applied pressure [14], or appropriate ion substitution (“chemical pressure effect”) [15]. We have to note that similar anomalous dependence of superexchange interaction on temperature was reported for single-chain $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films [13]. It was tentatively attributed to the effect of stress due to different thermal expansion coefficients of the films and the SrTiO_3 substrate. Our experimental data indicate that the anomalous

²⁾ Modification of the fitting line shape only weakly changes the temperature behavior of the line parameters. A model fit is, however, required in order to obtain quantitative information on, e.g., magnon lifetime, as it was done in refs. [10, 13].

temperature dependence of superexchange coupling could be an intrinsic property of Pr-based oxides.

It is seen from Fig. 3a that the linewidth of the two-magnon peak decreases upon sample cooling. This signals an increase of the magnon lifetime upon lowering the temperature (see ²). Despite the line narrowing, the integrated intensity of the two-magnon peak steadily increases with decreasing temperature with respect to the out-of-plane out-of-phase oxygen phonon of B_{1g} symmetry at 300 cm⁻¹ (Fig. 3c).

The driving force of the anomalous temperature dependence is the “metallization” of PrBa₂Cu₄O₈ below $T^* \approx 150$ K. Indeed, the two-magnon scattering peak shifts to lower frequencies and broadens upon doping [2]. For PrBa₂Cu₄O₈, recent transport and magnetic property studies [9, 16, 17] did show that its resistivity changes the behavior from semiconductor like to metal like upon cooling below T^* and optical reflectivity measurements [18] reveal pronounced increase of the free carrier density at the same temperature. It has been argued that the double Cu₂O₂ chains of PrBa₂Cu₄O₈ are presumably the key structural element responsible for the appearance of this effect [9]. The results of two-magnon scattering, which probes primarily short-range spin dynamics of the CuO₂ planes show, however, that contribution of planes is essential in determining the properties the low temperature phase of PrBa₂Cu₄O₈.

4. Conclusions

The polarized inelastic light scattering experiments on double-chain PrBa₂Cu₄O₈ microcrystallites reveal an anomalous temperature dependence of the two-magnon peak position and, correspondingly, the in-plane exchange coupling J , which diminishes upon cooling below $T^* \approx 150$ K. This experimental fact implies that not only the double Cu₂O₂ chains, but also the planes are essential in determining the properties of the low temperature conducting phase of PrBa₂Cu₄O₈.

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References

- [1] C. THOMSEN, in: *Light Scattering in Solids VI*, Eds. M. CARDONA and G. GÜNTHERODT, Springer-Verlag, Berlin 1991 (p. 285).
- [2] G. BLUMBERG, M. KANG, M.V. KLEIN, K. KADOWAKI, and C. KENDZIORA, *Science* **278**, 1427 (1997).
- [3] P.W. ANDERSON, G. BASKARAN, Z. ZOU, and T. HSU, *Phys. Rev. Lett.* **58**, 2790 (1987).
- [4] M. KAKIHANA, M. KÄLL, L. BÖRJESSON, H. MAZAKI, M. YASUOKA, P. BERASTEGUI, S. ERIKSSON, and L.-G. JOHANSSON, *Physica* **173C**, 377 (1991).
- [5] P. BERASTEGUI, L.-G. JOHANSSON, M. KÄLL, and L. BÖRJESSON, *Physica* **204C**, 147 (1992).
- [6] M. KÄLL, A.P. LITVINCHUK, L. BÖRJESSON, P. BERASTEGUI, L.-G. JOHANSSON, M. KAKIHANA, and M. OSADA, *Phys. Rev. B* **56**, 3590 (1996).
- [7] K.B. LYONS, P.A. FLEURY, J.P. REMEIKA, A.S. COOPER, and T.J. NEGRAN, *Phys. Rev. B* **37**, 2353 (1988).
- [8] M. YOSHIDA, N. KOSHIZUKA, and S. TANAKA, *Phys. Rev. B* **42**, 8760 (1990).
- [9] I. TERASAKI, N. SELJI, S. ADACHI, and H. YAMAUCHI, *Phys. Rev. B* **54**, 11993 (1996).
- [10] P. KNOLL, C. THOMSEN, M. CARDONA, and P. MURUGARAJ, *Phys. Rev. B* **42**, 4842 (1990).

- [11] G. BLUMBERG, P. ABBAMONTE, M.V. KLEIN, W.C. LEE, D.M. GINSBERG, L.L. MILLER, and A. ZIBOLD, *Phys. Rev. B* **53**, 439 (1996).
- [12] W.H. WEBER and G.W. FORD, *Phys. Rev. B* **40**, 6890 (1989).
- [13] N. DIECKMANN, M. RÜBHAUSEN, A. BOCK, M. SCHILLING, K.-O. SUBKE, U. MERKT, and E. HOLZINGER-SCHWEIBER, *Physica* **272C**, 269 (1996).
- [14] A.A. MAKSIMOV and I.I. TARTAKOVSKII, *J. Supercond.* **7**, 439 (1994).
- [15] T. UZUMAKI, K. YAMANAKA, N. KAMEHARA, and K. NIWA, *Jpn. J. Appl. Phys.* **29**, L1150 (1990).
- [16] A.P. LITVINCHUK and L. BÖRJESSON, in: *Proc. 15th Internat. Conf. Raman Spectroscopy*, Wiley & Sons, Chichester 1996 (p. 886).
- [17] H.D. YANG, J.-Y. LIN, S.S. WENG, C.W. LIN, H.L. TSAY, Y.C. CHEN, T.H. MEEN, T.I. HSU, and H.C. KU, *Phys. Rev. B* **56**, 14180 (1997).
- [18] A.P. LITVINCHUK, L. BÖRJESSON, C. THOMSEN, and P. BERASTEGUI, *J. Phys. Chem. Solids* **59**, 2000 (1998).