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Light scattering by magnons in Bi_2CuO_4 single crystals

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Abstract. The polarized Raman scattering spectra of Bi_2CuO_4 single crystals were measured at temperatures between 10 and 300 K. In addition to the Raman-active phonon modes, two new structures at 14 and 150 cm^{-1} appear at temperatures below 50 K. These modes, which are assigned as one- and two-magnon modes, have E_g symmetry and E_g and B_{1g} symmetry, respectively. Their temperature dependences agree well with previous results of antiferromagnetic resonance experiments.

1. Introduction

The discovery of the high-temperature superconducting oxides has led to rapidly increasing interest in studies of the properties of the whole series of CuO-based materials. Since most of these oxides have antiferromagnetic properties, special affinity has been expressed in studying their magnetic ordering. Among the vast group of CuO-based materials, Bi_2CuO_4 attracts special attention because of its interesting crystal structure and magnetic properties. This oxide has a tetragonal [1, 2] crystal structure with isolated CuO_4 square-planar units of Cu^{2+} ions which are stacked one on the top of another in a staggered manner along the *c* axis. Two different space groups have been reported for the crystal structure of Bi_2CuO_4: $I4$ [1] and $P4/ncc$ [2]. Recently, the crystal structure of this compound has been reinvestigated. On the basis of these results [3–5], as well as the Raman spectroscopy [6] results, it has been confirmed beyond any doubt that Bi_2CuO_4 crystallizes in the tetragonal system with $P4/ncc$ space group.

With reference to the magnetic structure of Bi_2CuO_4 there is also some controversy. In [7] it is stated that Bi_2CuO_4 is an oxide system which exhibits a linear-chain magnetic behaviour. On the contrary for the magnetic susceptibility data at low temperatures neither the uniform nor the alternating Heisenberg antiferromagnetic model can be fitted and the possibility of a spin-Peierls transition cannot be ruled out. On the other hand, recently published neutron spectroscopy results on the magnetic structure of Bi_2CuO_4 show that this crystal is rather a three-dimensional (3D) antiferromagnetic system with a tendency to anisotropic 2D magnetic behaviour [4]. Also, there is some controversy about the magnetic moment orientation of Bi_2CuO_4. In [3–5] the spin orientation is along the [001] direction but in [8] it is shown that the magnetic moment orientation is along the [100] direction.

The susceptibility versus temperature dependence of Bi_2CuO_4 shows a maximum at about 50 K, which shifts towards higher temperatures when the applied magnetic field increases [9]. Moreover, an additional maximum in the susceptibility curve at temperatures lower than 20 K has also been observed. The exact location and origin of this anomaly are not known. It is supposed that it originates from paramagnetic impurities [9], while, from x-ray or neutron spectroscopy measurements [3, 8], the existence of any structural phase transition at these temperatures has not been confirmed.

In our previously published paper [6] we discussed the polarized Raman spectra of Bi_2CuO_4 at room temperature and the far-infrared spectra of the ceramic samples. In this paper we measure the polarized Raman spectra of Bi_2CuO_4 single crystals at temperatures between 10 and 300 K. At temperatures below 50 K, two new peaks appear clearly: the first peak is at about 14 cm^{-1} with E_g symmetry and the second peak is at about 150 cm^{-1} with E_g and B_{1g} symmetry and does not disappear at temperatures above T_N ($\simeq$ 50 K). We assigned these modes as one- and two-magnon modes, respectively.

2. Experiment

Crystal growth experiments were carried out by a floating-zone technique associated with an ellipsoidal image furnace [10]. Polycrystalline feed rods 10 mm in diameter and 80 mm long were prepared by finely grinding Bi_2O_3 and CuO powders, isostatically presssing them under 1 t cm^{-2} in cylindrical rubber tubes and reacting them in air at 750 °C for 24 h.

Growth was started by establishing a molten zone between the feed rod and a seed obtained from first experiments where growth was initiated on polycrystalline pedestals. Seed orientation was facilitated by easy cleavage of Bi_2CuO_4 along [001]. Crystals were grown in air in the [001] direction at a rate of 1 cm h^{-1}, the feed rod and seed holder being counter-rotated at 30 rev min^{-1}.

The crystals that were obtained are typically 6–10 mm in diameter, depending on the descent rate of the feed rod, and several centimetres long. Growth was frequently perturbed by cracking and cleavage of the crystals along [001] during growth. More details about crystal growth and properties of samples used in this work can be found in [11].

The Raman spectra were excited by the 514.5 nm line of an argon ion laser (the average power was about 100 mW), focused to a line focus using a cylindrical lens. The geometry was of a back-scattering type with an aperture f of the collecting objective of 1:1.4. The monochromator used was a Jobin–Yvon model U-1000 with 1800 grooves mm^{-1} holographic gratings. As a detector, we used a Pelletier-effect-cooled RCA 31034 A photomultiplier with a conventional photon-counting system. The samples were held in a closed-cycle cryostat (Leybold, Germany), equipped with a low-temperature controller (Leybold model LTC-60) and evacuated by a turbopump.

3. Results and discussion

The polarized Raman spectra of Bi_2CuO_4 obtained from the (001) plane in the spectral range from 10 to 200 cm^{-1} are shown in figure 1. The full and broken curves represent Raman spectra at 10 K and 300 K, respectively. All frequencies given in the text correspond to the temperature of 10 K and they are denoted by arrows in the figures. Preliminary assignment of the phonon modes of Bi_2CuO_4 at room temperature has been given in our previous report [6] and we shall not discuss them here. We recall that the lowest-frequency modes originate from Bi atom vibrations while modes at around 130 cm^{-1} come from Cu atom vibrations along the z direction.

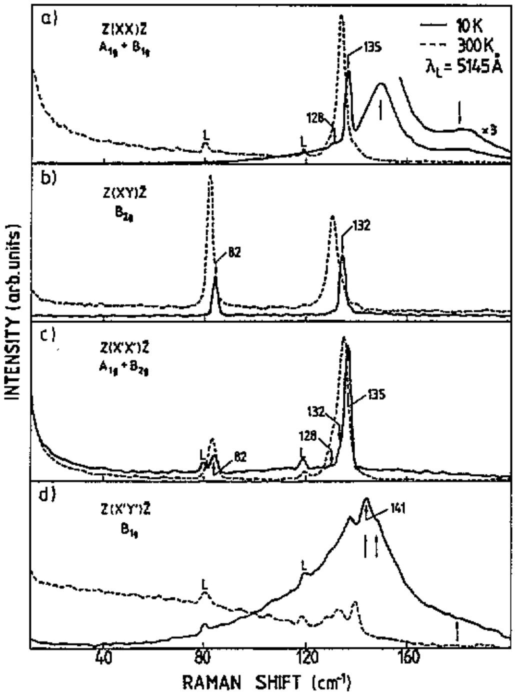

Figure 1. The Raman scattering spectra of Bi_2CuO_4 at 300 K (- - -) and 10 K (——): (*a*) $z(xx)\bar{z}$ polarization; (*b*) $z(xy)\bar{z}$ polarization; (*c*) $z(x'x')\bar{z}$ polarization; (*d*) $z(x'y')\bar{z}$ polarization. ($x\|[100]$, $y\|[010]$, $z\|[001]$; $x'\|[110]$, $y'\|[1\bar{1}0]$.)

The xx polarized spectra are shown in figure 1(*a*). This polarization permits the appearance of the A_{1g} and B_{1g} symmetry modes. In the given spectral region the A_{1g} mode at 135 cm^{-1} is clearly observed. As previously discussed [6], the B_{1g} modes have a very small intensity and they have not been observed until now. At 10 K, besides the mode-hardening effect of the A_{1g} mode, the new peaks (denoted by arrows) at 150 and 180 cm^{-1} appear. We shall discuss the nature of these structures later.

The depolarized spectra ($z(xy)\bar{z}$ configuration) which correspond to the B_{2g} symmetry are shown in figure 1(*b*). The two phonon modes at 82 and 132 cm^{-1} are clearly observed at both temperatures. On decreasing the temperature, no other modes were observed.

The spectra of the $z(x'x')\bar{z}$ configuration with A_{1g} and B_{2g} active modes are presented in figure 1(*c*). The mode frequencies are 82 cm^{-1} (B_{2g}), 128 cm^{-1} (A_{1g}), 132 cm^{-1} (B_{2g}) and 135 cm^{-1} (A_{1g}) and they harden on decreasing the temperature. As can be seen from figure 1(*c*), the two low-intensity modes at 128 and 132 cm^{-1} are masked by the high-intensity A_{1g} mode at 135 cm^{-1}. Because of that the mode assignment in figure 1(*c*) is obtained by comparing corresponding spectra from figure 1 and figure 2. In the $x'x'$ polarization no other modes were observed at low temperatures.

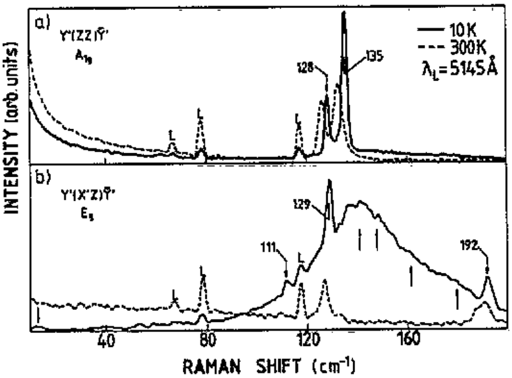

Figure 2. (*a*) Polarized and (*b*) depolarized Raman scattering spectra of Bi_2CuO_4 measured from the (1̄10) plane at temperatures of 10 K (——) and 300 K (- - -).

Finally, the depolarized spectra in the $z(x'y')\overline{z}$ configuration (B_{1g} symmetry modes) are shown in figure 1(*d*). In this polarization the peak intensities are of the same order as noise. We assigned the high-intensity peak at 141 cm^{-1} as the B_{1g} mode. Other features in these spectra are either plasma lines or 'leakage' of the A_{1g} modes. At $T = 10$ K the new broad structure is observed as in the case of figure 1(*a*) but centred at a frequency of about 140 cm^{-1}. It is also interesting to note that elastically scattered light has a higher-intensity background level at 300 K than at 10 K. We shall show later that this effect is due to the two-magnon scattering which can be seen even at a temperature of 300 K.

The Raman spectra from the (1$\bar{1}$0) plane are shown in figure 2. The zz polarization gives only the A_{1g} active modes. Two modes at 128 and 135 cm^{-1} are here resolved much better than in the case of the xx and $x'x'$ polarization because of the absence of modes other than A_{1g}.

The spectra of the $y'(x'z)\overline{y'}$ configuration (E_g symmetry modes) are presented in figure 2(*b*). In this configuration, besides the E_g modes at 111, 129 and 192 cm^{-1}, we observed a low-intensity mode at 14 cm^{-1} at 10 K, as well as a broad mode at about 140 cm^{-1} (as in figure 1(*d*)).

The $x'z$ and $x'y'$ polarized spectra at several temperatures are shown in figure 3 and figure 4, respectively. The inset in each figure gives the peak frequency of the corresponding mode as a function of the temperature. The 14 cm^{-1} mode, with E_g symmetry, completely disappears at a temperature of about 40 K while the 150 cm^{-1} mode, with B_{1g} and E_g symmetry, can be observed up to 300 K.

The appearance of the 14 cm^{-1} mode at a temperature below T_N together with its peak frequency dependence lead us to attribute this excitation to one-magnon scattering. Also, from the magnetic point group analysis [12], we found that the zone centre magnon mode of Bi_2CuO_4 has E_g symmetry.

The intensity of the 150 cm^{-1} mode decreases on increasing the temperature but the mode is still visible even at a temperature of about $6T_N$. This behaviour and the peak frequency dependence suggest that this mode is of a magnetic nature and that it could arise from the two-magnon scattering. The intensity of the one-magnon mode is approximately 200 times weaker than the intensity of the two-magnon mode

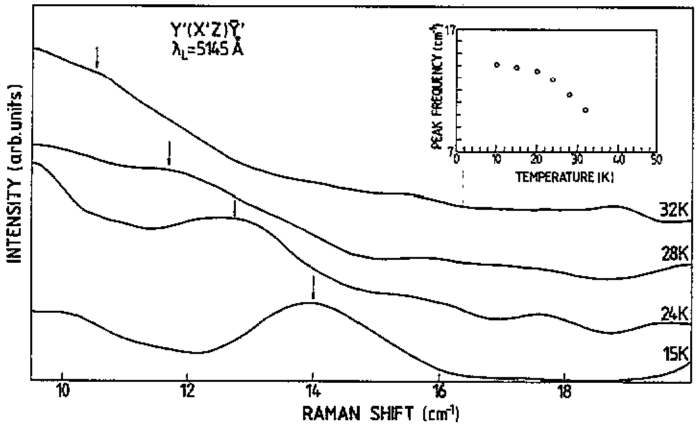

Figure 3. The Raman scattering spectra of Bi_2CuO_4 in the $y'(x'z)\overline{y}'$ polarization at several temperatures. The inset shows the one-magnon peak frequency dependence as a function of the temperature.

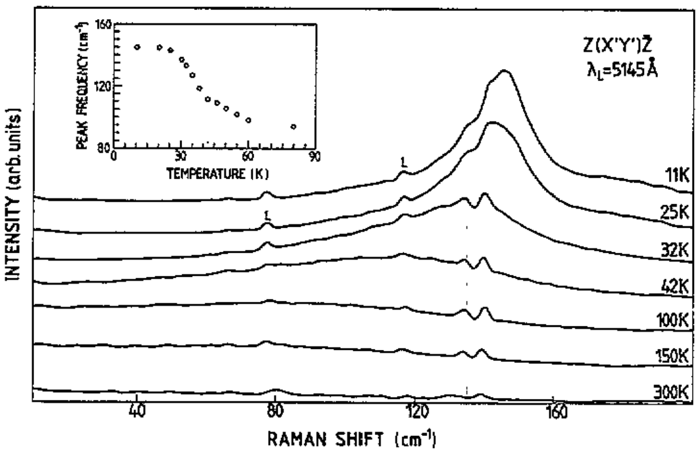

Figure 4. The Raman scattering spectra of Bi_2CuO_4 in the $z(x'y')\overline{z}$ polarization at several temperatures. The inset shows the two-magnon peak frequency dependence as a function of the temperature.

which is in agreement with the already-observed effect that the antiferromagnets with smaller $k = 0$ magnon frequency tend to be less efficient Raman scatterers [13].

Since the one-magnon process gives the Brillouin-zone-centre magnon frequency and the two-magnon process receives its strongest contribution from the zone-edge magnons, it is tempting to relate the features of the scattered light spectrum to the magnon dispersion relation. Unfortunately the full magnon dispersion curves of Bi_2CuO_4 are not measured. In [10], magnetic excitations in the magnetic ordered phase of Bi_2CuO_4 were investigated at 10 K using inelastic neutron scattering. The gap of 0.42 THz obtained at the centre of the Brillouin zone is in complete agreement with the one-magnon mode frequency at 14 cm^{-1} (figure 3, inset).

The shape of the two-magnon mode is very broad and it is different in different polarizations (see figures 1(*a*), 1(*d*) and 2(*b*)). We resolved four different peaks (denoted by arrows) at frequencies of about 140, 150, 160 and 180 cm^{-1}. The frequencies of these two-magnon peaks correspond to the values of the zone-edge magnons of 70 cm^{-1} (2.1 THz), 75 cm^{-1} (2.25 THz), 80 cm^{-1} (2.4 THz) and 90 cm^{-1} (2.7 THz). Unfortunately, the magnon dispersion curves are measured along the [100] and the [001] directions only below 2.2 THz and there are no results on Brillouin zone-edge magnons which determine the two-magnon scattering. Still, we believe that the highest-frequency magnon mode (180 cm^{-1}) originates from the X point of the Brillouin zone edge because the slope of the magnetic dispersion curve along the [100] direction is larger than that along the [001] direction. More accurate assignment of these peaks will be possible when the complete magnon dispersion curve is known; this is in progress [14].

Since we observed different two-magnon peak positions in different polarizations, it is necessary to include more than one exchange constant in the Heisenberg Hamiltonian. This proves the 3D character of the magnetic interaction in Bi_2CuO_4. A rough estimate of the exchange constant can be made if we approximate the magnetic interaction of Bi_2CuO_4 as one dimensional. Using the known relation between the Raman-peak energy of the two-magnon mode and the exchange coupling constant J [15], namely $E_{\text{two-mag}} = 2.7J$, we obtained $J = 52$ cm^{-1} (= 74 K). This value is close to the value already obtained by calorimetric measurements [7]. More detailed information could be obtained by considering the complete interaction Hamiltonian. These investigations are under way.

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