Optical study of antiferromagnetic single crystals $Y_{1-x}Pr_xBa_2Cu_3O_6$ in high magnetic fields

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Infrared measurements and linear-spin-wave calculations for single-crystal $Y_{1-x}Pr_xBa_2Cu_3O_6$ (x=0.0, 0.4, 1.0) in magnetic fields up to 30 T show that absorption features which have been ascribed to magnon excitations are very insensitive to the applied field. The substitution of Pr^{3+} for Y^{3+} leads to an additional absorption feature, which does have a strong field dependence. This excitation is assigned to an intermultiplet transition in the Pr^{3+} ion. The zero-field temperature dependence of this absorption shows clear evidence of an interaction between Cu and Pr spins. [S0163-1829(97)14117-0]

The cuprate materials order in a quasi-two-dimensional antiferromagnetic phase as mobile charges are removed. Neutron-scattering measurements have observed spin-wave excitations in La_2CuO_4 (Ref. 1) and $YBa_2Cu_3O_{6+\delta}$ (Ref. 2), yielding a fairly large in-plane exchange interaction $J\approx 1000$ cm^{-1} and also finding non-negligible intrabilayer exchange constants for $YBa_2Cu_3O_{6+\delta}$.[3] Raman measurements have observed two-magnon excitations in the 2000–4000 cm^{-1} region.[4] Investigations of single-layer and bilayer materials show that this behavior is a general feature of the insulating phase.

Infrared measurements below the charge-transfer gap of the semiconducting cuprates have shown a variety of weak midinfrared absorption features, some of which are possibly magnetic in origin.[5–7] In all materials, this midinfrared absorption is close to the energy of the two-magnon Raman scattering peak. The double-layer material $YBa_2Cu_3O_6$ has in addition a strikingly narrow absorption line at 1436 cm^{-1}, which is not seen in single-layer materials. This structure has been attributed to the excitation of a single magnon of the optical branch.[6]

If the Y^{3+} is replaced by a rare-earth ion a second spin system appears: the $4f$ electron configuration of the rare earth. Crystal field splitting of ground state and excited levels gives rise to new absorption features; these have been observed in $PrBa_2Cu_3O_y$ (y=6 and 7) and Pr_2CuO_4 by neutron spectroscopy and Raman scattering, respectively.[8–11] Pr substitution is particularly interesting because in the fully oxygenated phase the substitution destroys the superconductivity. Recent neutron-scattering measurements[12] have provided evidence for significant magnetic coupling between the Cu and Pr spin systems.

The magnetotransmittance measurements on the insulating $Y_{1-x}Pr_xBa_2Cu_3O_6$ system reported here find a strong field dependence of a peak at 2275 cm^{-1} that arises when Pr is present. This Pr-related feature is seen to interact with the antiferromagnetism of the CuO_2 system. In addition, we find a negligible shift with field of the sharp absorption line at 1436 cm^{-1} and of the possible two-magnon midinfrared absorption.

Our crystals were grown using a self-flux method described elsewhere[13,14] and were annealed either in UHV at 700 K for two days or in flowing argon at 950 K for four days to obtain undoped material. To obtain a good surface quality, the samples were etched for 3 min in 1% Br in ethanol solution prior to the measurement. The optical measurements were performed using a Fourier-transform spectrometer (Bruker IFS 113v) and (at zero field only) a grating spectrometer (Perkin-Elmer 16U). The frequency range was 700–12 000 cm^{-1} at zero field and 700–4000 cm^{-1} at high magnetic field. For the transmittance measurements in magnetic field, a light pipe was used to carry the infrared light through the bore of a resistive magnet. The field range was B=0–30 T. A bolometer detector was mounted at the end of the light pipe; both sample and detector were in a helium Dewar. The field dependence of the detector was calibrated by measuring an empty diaphragm at different magnetic fields. For certain measurements the normal to the (001) surface of the sample was oriented at an angle of 30° to the static field, enabling magnetotransmittance with an in-plane component of the field.

Figure 1 shows the 10 K optical conductivities $\sigma_1(\omega)$ for $YBa_2Cu_3O_6$ (YBCO), $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_6$ (YPBCO), and

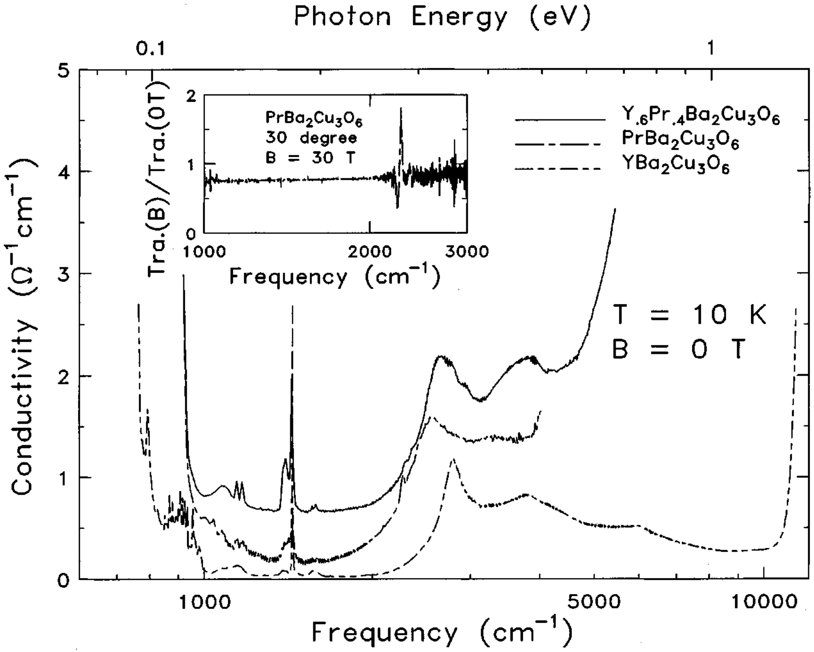

FIG. 1. The 10 K optical conductivities for $PrBa_2Cu_3O_6$ (short-long dashed line), $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_6$ (solid line), and $YBa_2Cu_3O_6$ (short-short-long dashed line). The inset shows the ratio of the 30 T to the 0 T transmittances $\mathcal{T}(30\ T)/\mathcal{T}(0\ T)$ for $PrBa_2Cu_3O_6$ in the 30° configuration ($T = 10$ K).

$PrBa_2Cu_3O_6$ (PBCO), calculated from the transmittance and reflectance.[7] The low-frequency range is dominated by multiphonon absorption, with two-phonon processes contributing up to about 1400 cm^{-1}. All three materials have a sharp absorption line at ~ 1436 cm^{-1}. With increasing Pr doping its spectral weight decreases by about a factor of 2 and its width increases by about a factor of 3. A second significantly broader and stronger feature occurs at 2795 (YBCO), 2640 (YPBCO), and 2560 cm^{-1} (PBCO). In single-layer materials a similar peak is found at higher energies.[5–7]

It is believed that the origin of these features is the antiferromagnetism of the CuO_2 planes. The two-magnon Raman line is close in energy to the 2500–2800 cm^{-1} midinfrared feature, suggesting that the latter has a similar origin. Two-magnon infrared absorption, however, requires an additional symmetry-breaking process. Several such processes have been proposed including disorder,[5] sidebands of a direct absorption (such as a *d*-*d* exciton),[5] an optical phonon,[15] and buckling of the layers plus spin-orbit coupling.[6]

We focus now on the additional absorption feature, at 2275 cm^{-1} (PBCO) and 2289 cm^{-1} (YPBCO), which is absent in YBCO (see Fig. 1). Its energy is in the range where transitions from levels of the ground state to levels of the first excited state in the Pr^{3+} ion can occur.[16] The inset shows the ratio of transmittance at 30 T to that at zero field for $PrBa_2Cu_3O_6$, with the sample mounted in the 30° configuration. A change can be seen at 2275 cm^{-1}, whereas an almost constant ratio is obtained outside this region, implying that the other features in the spectrum show no noteworthy field dependence.

Figure 2 displays the magnetic field and temperature dependence of this 2275 cm^{-1} feature. The right panel shows the transmittance $\mathcal{T}$ of $PrBa_2Cu_3O_6$ at fields between 0 and 30 T, applied along the c axis. The inset shows $\mathcal{T}$ for $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_6$ at 0 and 30 T. With increasing field, the absorption dip splits in two, with one line that shifts down and a weaker one that shifts up (and which really can be seen only above 8 T). A much weaker feature can be seen at 2095 cm^{-1}, also due to Pr doping, which moves with field by a smaller amount. There appears to be a change in the shape of another weak feature at 2350 cm^{-1}, but the frequency where the feature appears does not change with field. In the left panel the transmittance is plotted over the same frequency range for temperatures between 10 and 390 K. Both the 2095 and the 2275 cm^{-1} absorptions are almost constant in frequency, but broaden and weaken with increased temperature.

We fitted the line shape in $\ln(1/\mathcal{T})$ using two oscillators to describe the field and temperature dependence of the absorption feature and three broad oscillators to fit the background (not changed with field). Figure 3, upper panel, shows the 5 K result for PBCO with $B\|c$ and 30° configuration and for YPBCO with $B\|c$. In PBCO the oscillator strength is distributed about 35% into the upper branch and 65% into the lower branch. The feature is weaker in YPBCO and only the red-shifting branch can be discerned.

The shift with field is linear, with different slopes for the lower and upper branch. The slopes in the 30° configuration are both reduced by a factor $\cos 30° = 0.87$, indicating that the field component perpendicular to the planes is responsible for the magnetic field dependence. That the absorption frequency is close to the first excitation band of the Pr^{3+} ion and that it has a strong field dependence are evidence for an intermultiplet transition in the Pr^{3+} ion.[17,18] The free Pr^{3+} ion has a $4f^2$ configuration with a ninefold degenerate ground-state $^3H_4$ multiplet and an elevenfold degenerate first excited-state $^3H_5$ multiplet. Whereas this intermultiplet transition of the free Pr^{3+} accounts for the approximate position of the absorption, the interaction with the environment is crucial for its magnetic field and temperature behavior. Due to the crystalline environment the quantum number J_z ceases to be good (J is the total angular momentum) and crystal quantum numbers μ can be used to classify the crystal field energy levels.[17] For D_{4h} symmetry we obtain $\mu = 0, \pm 1$ with five nondegenerate states and two doubly degenerate states in the ground level and in addition a doubly degenerate state in the first excited level. Here, we consider the optical tran-

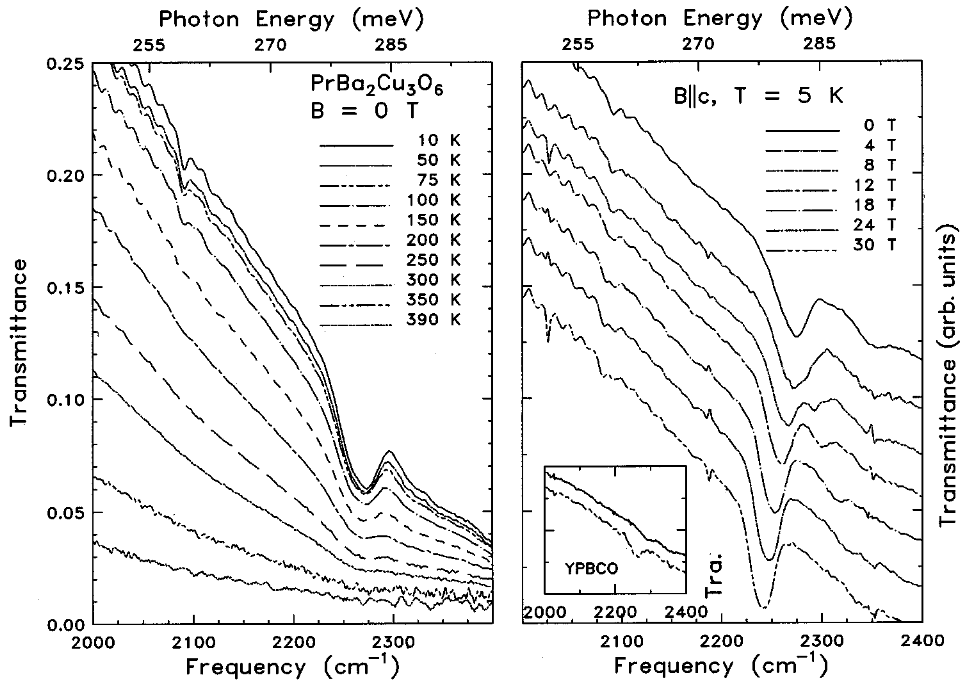

FIG. 2. The transmittance of $PrBa_2Cu_3O_6$ over 2000–2400 cm^{-1}. The right panel shows the field dependence up to 30 T. Here the curves have been displaced from one another for clarity and $\mathcal{T}$ is in arbitrary units. The inset displays the result for $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_6$ at 0 and 30 T. The left panel shows the temperature dependence between 10 and 390 K at zero field for $PrBa_2Cu_3O_6$.

sition between the ground state (g) to the first excited state (e) with both levels splitting in magnetic field. The transitions are between $\omega_g-\gamma_g\mu_B B$ to $\omega_e\pm\gamma_e\mu_B B$ with the zero-field transition $\omega_e-\omega_g$. A fit to our data yields $\gamma_g=1.01\pm0.05$ and $\gamma_e=3.5\pm0.1$. These splitting factors γ_i are analogous to the Landé factors g_J (Ref. 19) times the respective value of J_z. They can be understood as linear combinations of J_z levels ±1, ±3, and ±5.

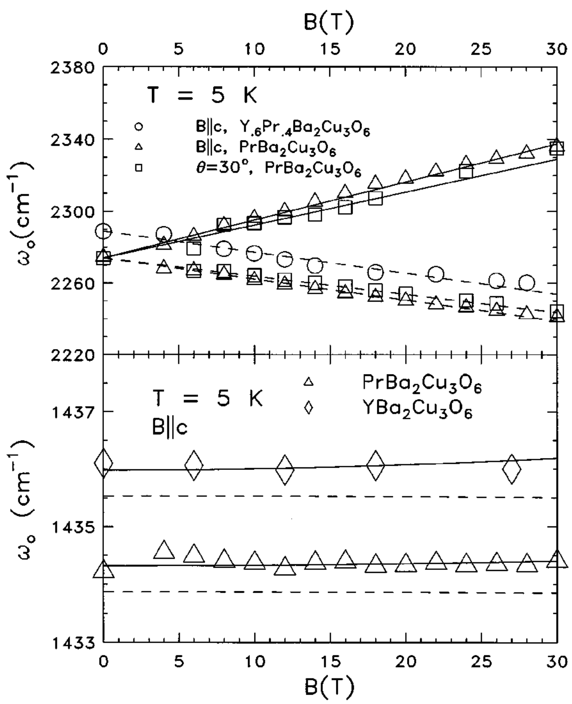

FIG. 3. Upper panel: Field dependence of the intermultiplet transition in the Pr^{3+} ion for $PrBa_2Cu_3O_6$ for $B\|c$ and 30° to the normal and for $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_6$ for $B\|c$. The dashed and solid lines show linear fits. Lower panel: The frequency of the absorption line at 1436 cm^{-1} is plotted as a function of field for $B\|c$ at $T=5$ K. The solid line (mainly out-of-plane mode) and dashed line (mainly in-plane mode) are theoretical calculations.

The interaction of the Pr^{3+} moments with the CuO_2 spin system is strongly evident in the temperature (T) dependence of this absorption. Figure 4 shows the normalized oscillator strength of the absorption N_{eff}/N_0 as a function of T obtained from two independent data evaluations, i.e., from the oscillator strength of a Lorentzian fit and from sum-rule calculations for $\sigma_1(\omega)$.[20] The dashed line shows the expected behavior if depopulation of the lowest crystal-field levels determines the T dependence. This calculation, which is based on a Boltzmann distribution of the local crystal-field levels given by Hilscher *et al.*,[10] cannot satisfactorily describe the T dependence. Even if we assume that intermediate levels or shifts of these levels would be present, no adequate fit can be obtained. The solid line shows a mean-field ansatz $N_{\mathrm{eff}}\propto\sqrt{1-T/T_N}$, with T_N the Néel temperature of the Cu spins. This assumption describes the situation well, implying an interaction between Cu and Pr spins in the mate-

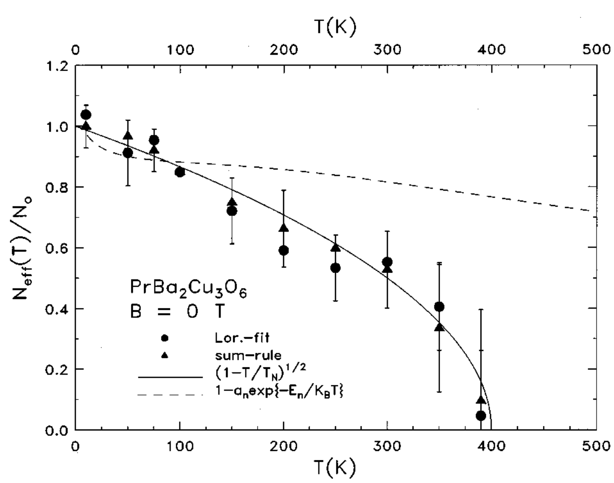

FIG. 4. Temperature dependence of N_{eff}/N_0 for the intermultiplet transition at $B=0$ T, obtained in two different ways. The dashed line is a fit using the Boltzmann distribution, the solid line a fit taking T_N(Cu spins) into account.

rial. This result is in agreement with the neutron-scattering study of Boothroyd *et al.*[12] and shows that the interaction continues above the 10–20 K ordering temperature of the Pr spins. The hybridization of the Pr $4f$ orbitals with the oxygen $2p$ orbitals may favor the Pr-Cu interaction via superexchange. It is interesting to speculate that a similar hybridization is responsible for the absence of superconductivity in $PrBa_2Cu_3O_7$.

We now turn to the sharp line at 1436 cm^{-1}, which has been assigned to a single optical magnon absorption.[6] Despite the magnon interpretation only a very small effect of applied magnetic field is expected for the feature, due to the anisotropy between the susceptibility for spins perpendicular and (anti)parallel to the applied field direction, which favors a spin flop. Spin-flop transitions have been reported for $Sr_2CuO_2Cl_2$,[21] $YBa_2Cu_3O_6$,[22] and La_2CuO_4.[23] Above the spin-flop field ~ 6 T the spins are aligned almost perpendicular to the applied field, slightly canted in the field direction with a tilt angle φ. In a simple picture the energy of a single magnon excitation in a perpendicular field B scales with $g\mu_B B \sin\varphi$ and the tilt angle can be estimated as $\varphi \approx g\mu_B B/8J$.[24] With $B=30$ T, i.e. $g\mu_B B \approx 28$ cm^{-1}, and $J \approx 1000$ cm^{-1}, this leads to an energy shift of about 0.1 cm^{-1}, much smaller than the 7 cm^{-1} width of the 1436 cm^{-1} peak. A similar result is obtained from linear spin-wave theory (LSW), assuming a value of $J_{12}/J \approx 0.55$ for the ratio of the intrabilayer and in-plane exchange coupling constants in order to obtain a single optical magnon at 1436 cm^{-1} and an anisotropy constant $\alpha_D = 0.00014$ in order to reproduce the 36 cm^{-1} gap of the out-of-plane acoustic magnon for YBCO.[25]

We fitted the sharp absorption line at 1436 cm^{-1} using a single Lorentzian oscillator to fit the line shape in $\ln(1/\mathcal{T})$. Two additional broad oscillators were used to describe the background and the changes in the overall transmittance in field. A fourth (field-independent) oscillator was fitted to the 1380 cm^{-1} multiphonon structure. In Fig. 3, lower panel, we plot the fitted frequency for the sharp absorption feature in YBCO and PBCO for applied field $B \| c$ together with the LSW result. The upper (lower) branch contains 70% (30%) out-of-plane character. Similar results are obtained in the 30° configuration. The symbol size shows the experimental error and the uncertainty in the fit. Thus, the experimental results neither really support nor exclude an interpretation as a single optical magnon. Other measurements on YBCO at magnetic fields up to 16.5 T ($B \| ab$ and $B \| c$) do not find a measurable shift of this absorption line.[26] Recently, two independent neutron-scattering groups reported the observation of the single optical magnon in YBCO at about 550 cm^{-1}.[3] Hence, the question of the origin of this peculiar sharp infrared feature still has to be understood.

In the case of the probable two-magnon midinfrared absorption at 2500–2800 cm^{-1}, there is in first order no field dependence expected, independent of the local interaction between the two magnons.[27] Indeed, we see no effects in our spectra (inset of Fig. 1).

In summary we have measured magnetotransmittance in the semiconducting limit of bilayer cuprates. The negligible field dependences of features that have been associated with magnons in the CuO_2 planes[5,6] are in accord with theoretical expectations for such features, although, of course, a nonmagnetic origin cannot be ruled out.

We also observed a strong field dependence in a Pr-related feature that can be understood in terms of an intermultiplet excitation process. The temperature dependence of this excitation shows evidence for an interaction between Pr and Cu spins, in agreement with recent neutron results.[12]

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