Resonant X-Ray Raman Spectra of Cu *dd* Excitations in $Sr_2CuO_2Cl_2$

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We present resonant x-ray Raman scattering results on $Sr_2CuO_2Cl_2$, a model compound for high-T_c superconductors. We demonstrate that the dd excitations can be observed and show that the polarization dependence can be used to identify the dd excitations. We find the transition from the $d_{x^2-y^2}$ ground state to the d_{xy} excited state at 1.35 eV and to the degenerate d_{xz} and d_{yz} excited states at 1.7 eV. From analysis of the polarization dependence we conclude that the $d_{3z^2-r^2}$ orbital energy is at 1.5 eV and not in the midinfrared (0.5 eV) as recently suggested. We use recent theoretical arguments to show that the $d_{3z^2-r^2}$ excitation is accompanied by a local spin flip resulting in a shift upwards of 0.2 eV due to the exchange interaction with the neighboring spins. [S0031-9007(98)06273-5]

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Resonant x-ray Raman (RXR) spectroscopy has the makings of a powerful technique to study the elementary excitations in solids. Using excitation energies at specific core-level thresholds one can identify the excitations and determine their atomic origin. As was shown recently, one can even observe local spin flip excitations (and thus measure superexchange interactions) by choosing core-level resonances with strong spin-orbit coupling [1]. In this Letter we present the first RXR results on $Sr_2CuO_2Cl_2$, an insulating model compound for the high-T_c's, to determine the dd and accompanying spin flip excitations.

The energies of the lowest excitations in the Cu-based superconductors are basic quantities of interest in the ongoing struggle to determine the underlying electronic structure and elementary excitations. The energies of the local on-site dd excitations have been a topic of debate recently. The suggestion that some of these might occur at energies as low as 0.5 eV [2] reopens the question as to their importance in the so-called midinfrared part of the optical spectrum which is believed by some to be directly involved in the mechanism for high-T_c superconductors [3,4]. These dd excitations are not dipole allowed and therefore are rather weak in optical absorption spectroscopies. Recently, however, the highly stoichiometric and pure $Sr_2CuO_2Cl_2$ has provided the possibility to study also these weak transitions. It is generally accepted that in the ground state the $3d$ hole on Cu is in a $d_{x^2-y^2}$ orbital allowing for three local dd excitations in the local square-planar D_{4h} symmetry to the d_{xy}, the degenerate d_{xz}, d_{yz}, and the $d_{3z^2-r^2}$ states. The optical studies revealed a sharp feature starting at 0.4 eV followed by a rather wide absorption region which was suggested to be due to transitions to $d_{3z^2-r^2}$ local states [2]. Lorenzana *et al.* objected to this assignment and suggested that the very sharp structure at 0.4 eV was due to a phonon assisted two magnon absorption and supported this claim with theoretical calculations [5]. They, however, were unable to explain the intensity of the rather broad higher energy shoulder, which left open the possibility that this structure could be the transitions to $d_{3z^2-r^2}$ states. Also recent detailed Raman studies have been unable to find the $d_{3z^2-r^2}$ states at energies above 1 eV finding only the d_{xy} states at 1.35 eV [6,7]. Using resonant x-ray Raman spectroscopy we locate the d_{xy} and $d_{xz,yz}$ states and present strong evidence that the $d_{3z^2-r^2}$ excitation is around 1.7 eV.

By choosing x-ray energies at the Cu $3p$ resonances (around 75 eV) we achieve elemental specificity for local excitations on copper. We probe specifically the dd excitations by the transition sequence $3p^6 3d^9 \rightarrow 3p^5 3d^{10} \rightarrow 3p^6 3d^9$. These dd excitations are fully allowed, and their intensities can be calculated. The x-rays in this energy region have a penetration depth of about 1000 Å, so that the method is bulk sensitive. Only recently has the resolution of RXR spectroscopy become sufficiently high to study valence-valence excitations. Molecules and wide-band solids have attracted considerable interest [8], but the method has also been used to study charge-transfer excitations in correlated systems [9] and dd excitations in MnO [10].

Tanaka and Kotani were the first to study resonant x-ray Raman spectroscopy on cuprates theoretically [11]. They calculated the x-ray emission spectrum of CuO and La_2CuO_4 at the Cu L_3 resonance, and concluded that the energies of dd excitations can be measured by this method. Ichikawa *et al.* [12] measured the predicted difference for these two copper compounds. A polarization-dependent resonant study was done by Duda *et al.* [13], also at the L_3 $(2p_{3/2})$ resonance. But at these high energies (930 eV), it is difficult to achieve a combined resolution of monochromator and spectrometer better than

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1 eV, which is necessary to resolve low-energy excitations. That is much easier at the Cu $M_{2,3}$ $(3p)$ resonance around 75 eV, where we achieved a combined resolution of 0.2 eV in this first experiment. Theoretically, there is little difference between the Raman spectra at the $L_{2,3}$ and the $M_{2,3}$ edges. The nonresonant $M_{2,3}$ emission spectra of cuprates in Ref. [14] are affected by the 1.5 eV core-hole lifetime broadening, but the lifetime does not affect the resolution of resonant x-ray Raman spectroscopy for the same reasons it does not affect the resolution of resonant photoemission.

The experiment was performed at beam line 7 of the Advanced Light Source (ALS) at Berkeley. The synchrotron was running at an electron beam energy of 1.5 GeV. At this setting the undulator can go down in energy to approximately 70 eV. The undulator and monochromator combination produced a small intense spot of x-ray with an energy resolution of about 0.1 eV. The Raman spectra were recorded by a grazing-incidence grating spectrometer. We used a grating with 300 lines/mm with a radius of 3 m. A slit width of 30 μm gave a resolution of 0.2 eV, which also determined the resolution of this experiment (the width of the elastic peak).

The growth of the $Sr_2CuO_2Cl_2$ samples by the traveling solvent floating zone technique is described elsewhere [15]. As the experiments are not surface sensitive, the samples were cleaved *in situ* or just before introduction into vacuum. The sample quality was checked by the oxygen $1s$ x-ray absorption spectra. The polarization dependence of the total photoelectric current (surface sensitive) was similar to that of the x-ray fluorescent yield.

The spectra were recorded in two different geometries. In both cases the detector was placed in a direction perpendicular to the incident beam, either in the plane of the synchrotron orbit or perpendicular to it. The first geometry (horizontal position of the detector) has the advantage that the elastic peak is minimized (no Rayleigh scattering in the direction of the electrical field vector of the incident radiation). But the second geometry (vertical) is more suitable for determining the polarization of the scattered radiation from our two-dimensional sample. As inelastic scattering at the Cu p edges occurs only via excitation to the unoccupied $3d_{x^2-y^2}$, we want to keep the CuO_2 planes parallel with the polarization of the incident radiation. This is done by rotating the sample's normal from near perpendicular incidence (so that the vertical detector measures radiation at grazing exit angles with both x, y and with z polarizations) to nearly vertical (so that the detector measures only emission with x, y polarization). The rotations in this second (vertical) geometry are shown in the insets of Fig. 1.

Figure 1 shows the x-ray Raman spectra with the excitation energy at 74 eV, which is the Cu $3p_{3/2}$ (M_3) resonance. The spectra are normalized to the elastic peak, which is also shown reduced by a factor of 200. This elastic peak has a full width at half maximum of 0.2 eV, which is the resolution of this experiment. However, the tail of the strong elastic peak makes it impossible to observe excitations at energies smaller than about 0.5 eV. We observe clear sharp features between 1 and 2 eV energy loss, features that can be assigned to dd excitations on Cu^{2+}. Tanaka and Kotani predicted also charge-transfer peaks around 5 eV [11], but those are hardly seen at the L_3 resonance either [12,13], and must be weaker than predicted.

The intensity of the Raman spectrum is highest near grazing incidence (normal emission), and decreases when the sample is turned towards normal incidence. The decrease is caused by the combined effect of increasing penetration depth closer to normal incidence and increased absorption of emission towards the spectrometer. Clearly, it would be desirable to have samples with faces parallel to the c axis, to measure a stronger z-polarized signal. A very smooth surface is needed to avoid an excessively strong elastic peak.

Two inelastic peaks are resolved in Fig. 1, one around 1.35 eV and the other around 1.8 eV. The relative intensity of these peaks changes with angle. The peak at 1.35 eV becomes strongest closer to normal emission. Clearly this peak is polarized in the Cu-O plane, and the assignment to transitions to the xy orbital seems unavoidable. The peak at 1.8 eV must then be assigned to the xz and yz orbitals. This leaves one dd excitation unaccounted for, namely, the $3z^2 - r^2$ transition. Of

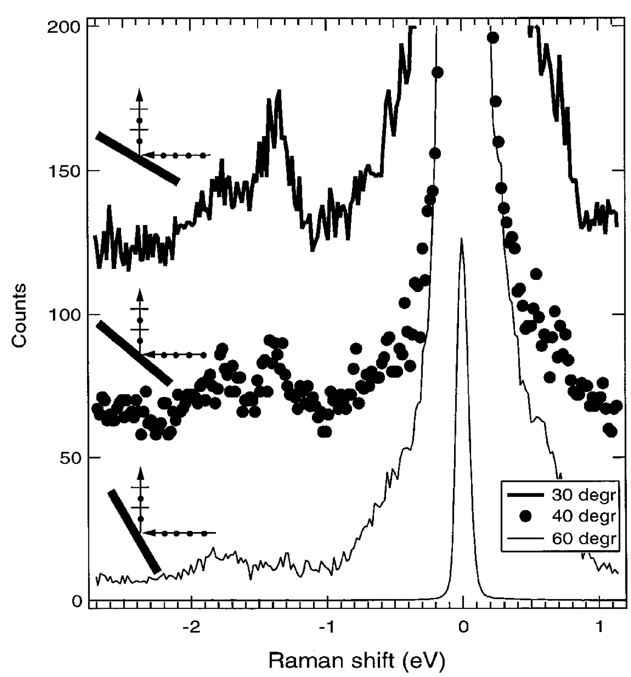

FIG. 1. Polarization-dependent x-ray resonant Raman spectra at the Cu M_3 resonance (74 eV). The angle between the emission direction and the sample normal is 30°, 40°, and 60°, from top to bottom. The last spectrum is also shown reduced by a factor of 200.

course, it might be hidden at low energies under the tail of the elastic peak. But if the splitting of the xy and xz, yz orbitals is 0.4 eV as in our assignment, one would expect the splitting between the $x^2 - y^2$ and the $3z^2 - r^2$ orbitals to be several times larger.

A calculation of relative intensities is necessary to understand why the $3z^2 - r^2$ peak is not seen in our spectra. The procedure is straightforward. As in the case of MnO [10], we use the Kramers-Heisenberg formula for inelastic scattering. In the present case of Cu^{2+}, the intermediate states have a filled $3d$ shell so that only six intermediate states need to be considered: four with a $3p_{3/2}$ hole ($m_j = 3/2, 1/2, -1/2, -3/2$) and two with a $3p_{1/2}$ hole ($m_j = 1/2, -1/2$). Interference plays a role because the $3p$ spin-orbit separation is comparable to the lifetime width. Selection rules and angular-overlap integrals determine the relative intensities of the final states. Unlike the case of MnO, the crystal field needs to be taken into account. The eigenfunctions in a crystal field are linear combinations of the atomic $3d$ Y_{lm} orbitals with well-known ratios, which are independent of the strength of the crystal field. Model calculations have been done on a Cu^{2+} atom in tetragonal symmetry with an exchange field along the z axis [1]. The results show that the $3z^2 - r^2$ peak is weak and that it is only allowed for spin flipped final states, so that this weak peak is spread out and shifted to higher energy by the exchange interaction and the excitation of magnons. But even with its calculated low intensity this peak cannot be hidden under the peak at 1.35 eV. The strong angle dependence of the relative intensities can only be reproduced by assuming that the $3z^2 - r^2$ transition contributes to the peak at 1.7 eV. Figure 2 shows spectra calculated with the following parameters: $10Dq_{xy} =$ 1.35 eV, $E(xz, yz) = E(3z^2 - r^2)$1.7 eV, and a spin flip energy of 0.2 eV.

The low Raman intensity made it difficult to investigate its energy dependence in detail, but a first result is clear enough to be presented. Figure 3 shows two spectra taken at the M_3 and at the M_2 edges in the horizontal position of the detector. The x-ray emission was measured in the direction of the **E** vector of the incident x rays, at an angle of 40° to the sample normal. The M_3 spectrum agrees with the middle trace of Fig. 1, but the M_2 spectrum is rather different. The intensity at 1.7 eV is relatively much lower, and there is extra intensity around 2 eV. Theory indicates that the intensities near the M_2 edge are sensitive to the exact excitation energy, because of interference with the M_3 path. The calculations reproduce this difference. The extra intensity around 2 eV at the M_2 resonance is due to spin flip states. They have a relatively larger intensity at the $3p_{1/2}$ than at the $3p_{3/2}$ intermediate state because of the $\Delta J = 0, \pm 1$ selection rule. This makes sure that the $m_j = 3/2$ intermediate state of opposite spin cannot be reached from the ground state. But at $3p_{1/2}$, both intermediate states ($m_j = 1/2, -1/2$) are populated, and there are relatively more spin flips in the excitation step [1].

Our observation of an in-plane polarized Cu dd excitation at 1.35 eV matches perfectly with a large-shift Raman peak observed by laser spectroscopy. Using photon energies around 3.5 eV, Salamon *et al.* [6,7] observe a loss peak with a polarization dependence characteristic for excitation to $3d_{xy}$ final states. Its energy dependence on the Cu-O bond length would predict a d_{xy} transition at 1.35 eV for 1.986 Å, the in-plane Cu-O bond length in $Sr_2CuO_2Cl_2$ [16]. We can also compare with data of $3d$ orbital energies in K_2CuF_4 [17] and in the square-planar $CuCl_4^{2-}$ ion [18]. Table I shows that the oxychloride is intermediate between these two other cases. One can also compare with the optically observed dd excitations in La_2NiO_4, where the tetragonal distortion is smaller [19].

In the controversy over the assignment of features in the optical spectra of high-T_c cuprates and the energy of the lowest electronic excitations, our results support a different assignment than that given by Perkins *et al.* [2].

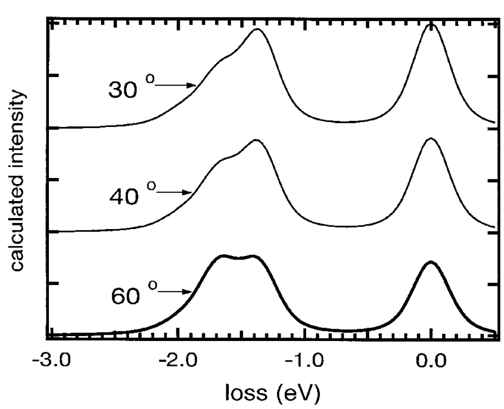

FIG. 2. Model calculation of the angle dependence at the M_3 resonance.

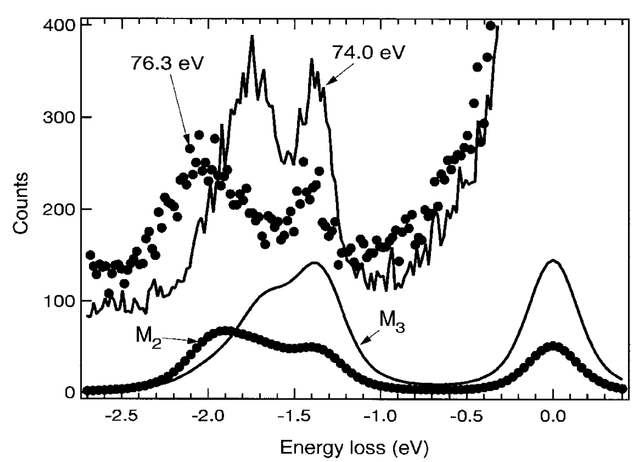

FIG. 3. X-ray resonant Raman spectra at the Cu M_3 and M_2 resonances (74 and 76.3 eV). The emission direction is in the direction of the incident polarization and makes an angle of 40° with the sample normal.

TABLE I. Energies in eV of the $3d$ orbitals of different square-planar coordinated Cu^{2+} ions.

Orbital	K_2CuF_4 [a]	$Sr_2CuO_2Cl_2$ [b]	$(CuCl_4)^{2-}$ [c]
xy	1.17	1.35	1.55
xz, yz	1.51	1.7	1.77
$3z^2 - r^2$	1.03	1.5	2.1

[a]Ref. [17]. [b]This work. [c]Ref. [18].

They assign a strong shoulder at 1.5 eV in the optical absorption of $Sr_2CuO_2Cl_2$ to $d_{x^2-y^2} \rightarrow d_{xy}$ transitions, but our x-ray and Salamon's laser Raman spectra [6,7] establish 1.35 eV as the energy for this excitation. Maybe this transition is responsible for the weak structure just below 1.4 eV in the optical spectrum [2]. Perkins *et al.* [2,20] assign a feature around 0.5 eV to $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$ transitions. Although we do not directly observe this transition (calculations indicate that it is relatively weak), such a low value would be inconsistent with a separation of 0.4 eV between the $3d_{xz(yz)}$ transitions and the $3d_{xy}$ peak. The splitting between the $d_{x^2-y^2}$ and the $d_{3z^2-r^2}$ should be at least 2 or 3 times as large in crystal or ligand field theory.

In conclusion, the new method of resonant x-ray Raman spectroscopy was used to study Cu dd excitations, using the Cu M_{23} resonance at 75 eV, with a resolution of 0.2 eV. We observe a peak at 1.35 eV, which on the basis of polarization dependence is assigned to the xy transition. At higher energies (1.8 eV on the M_3 resonance, 2.0 eV at the M_2 resonance) we find peaks which are assigned to xz, yz orbitals. The difference is due to different probabilities of magnon excitation. The controversial $3z^2 - r^2$ transition is not resolved, which can be explained by its low intensity according to theory. By comparing with calculations of the polarization dependence, we conclude that it is hidden under the $d_{xz,yz}$ structure at 1.8 eV, shifted 0.2 eV upward by a spin flip excitation.

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