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Energy and Polarization Dependence of Resonant Inelastic X-ray Scattering in Nd_2CuO_4

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We report the energy and polarization dependence of resonant inelastic x-ray scattering from Nd_2CuO_4. An energy loss feature at $\sim$ 6 eV is observed in the vicinity of the Cu K-edge. Numerical calculations based on the Anderson impurity model identify this as a charge transfer excitation to the anti-bonding state. The incident polarization is shown to select the intermediate states participating in the resonance process. Resonances are observed at 8990 eV and 9000 eV with the incident polarization perpendicular and parallel to the CuO planes, respectively. In contrast to our single-site model calculations, no resonances are observed associated with the $\underline{1s}3d^{10}\underline{L}$ intermediate states, suggesting non-local effects play a role.

The use of resonant inelastic x-ray scattering in the hard x-ray regime as a probe of charge transfer excitations has recently been shown to offer the potential for significant advantages over more traditional experimental techniques [1–4]. These advantages include; bulk-like penetration, element specificity and a charge-neutral scattering process. This latter fact means that there are no final state effects (i.e. those due to the presence of a core-hole in the final state) and it eliminates charging problems, facilitating the study of insulators.

Resonant enhancements, first observed in the hard x-ray regime in NiO [1], are significant because the non-resonant inelastic x-ray scattering cross-section is in general small, and only low-Z materials may be studied. Kao *et al.* discovered that on tuning the incident photon energy through the Ni K-edge, an enhancement on the order of a factor of 50 was observed in the inelastic scattering. Such enhancements offer the exciting possibility of allowing the study of more complex materials, in particular the high-Tc cuprates. However, they bring with them the disadvantage of a significantly more complicated cross-section, and much experimental and theoretical work remains to be done to fully understand the scattering process.

In this paper, we review our recent work on Nd_2CuO_4 in which a charge transfer excitation at 6 eV was observed with the incident photon energy tuned to 8990 eV, and explain in more detail the results of the numerical calculations used in interpreting this work. In addition, we report preliminary results of studies of the polarization dependence of the scattering process. These show that the intermediate state may be selected through the relative alignment of the incident polarization and the copper oxide planes. Resonances associated with $1s \rightarrow 4p_\pi$ and $1s \rightarrow 4p_\sigma$ transitions are thus resolved. Full results and analysis of this latter work will appear in a forthcoming paper [5].

The experiments were performed at two wiggler sources at the National Synchrotron Light Source, beamlines X21 and X25. The initial work [2], performed at X21 utilized a four bounce monochromator comprised of two channel cut Si(220) crystals. The incident resolution was 0.2 eV and the flux delivered on the sample was 5×10^{10} photons s^{-1}. The horizontally scattered radiation was collected by a spherically bent Si(553) analyzer and the overall energy resolution was a Gaussian of 1.9 eV full-width-at-half-maximum (FWHM), as measured by the quasi-elastic scattering from the sample. The sample was oriented such that the momentum transfer was along the c-axis, that is the incident polarization was largely perpendicular to the copper oxide planes [2]. In the second set of experiments [5], performed at X25, a vertical scattering geometry was utilized. In this case, with the momentum transfer again along the $\hat{c}$-axis, the incident polarization was entirely within the plane of the CuO sheets. For these latter measurements, a double crystal Si(111) monochromator was used with an incident energy resolution of 2.2 eV (FWHM), which delivered a flux of 5×10^{11} photons s^{-1}. The same analyzer set-up as in the earlier experiments was used, and the overall energy resolution was 2.3 eV (FWHM). For all results reported in this paper, the magnitude and direction of the momentum transfer was the same; $q = 4.6\mathring{A}^{-1}$, parallel to the $\hat{c}$-axis. The same sample was used in all measurements. It has a mosaic of 0.014° FWHM and is in the form of a platelet, 20mm x 10mm x 0.1mm with a c-axis surface normal.

The data of fig. 1, show a series of energy loss scans taken at different incident energies. A feature of constant energy loss of $\approx$ 6 eV is observed with the incident photon energy around 8990 eV. These data were taken in the horizontal scattering geometry, i.e with the incident polarization largely perpendicular to the ab plane ($\epsilon \perp ab$). The sloping background is due to the nearby $K\beta_5$ emission line.

The amplitude of the 6 eV feature was obtained as a function of incident energy by fitting such scans to a Gaussian of fixed position. The results of these fits are shown in fig. 2 (bottom half, open circles). A resonance is observed with a peak around 8990 eV.

In the top half of fig. 2, the absorption spectrum for Nd_2CuO_4 is shown. It exhibits features at 8983, 8990, 8995 and 9002 eV, which are associated with two sets of dipole transitions [6–8]. The first two features (lower energy pair) result from $1s \rightarrow 4p_\pi$ transitions ($4p$ orbitals perpendicular to the copper oxide sheets), the second two from $1s \rightarrow 4p_\sigma$ transitions (in-plane $4p$ orbitals).

The data of fig. 2 show that in the horizontal scattering geometry, ($\epsilon \perp ab$) the resonant enhancement is associated with the $1s \rightarrow 4p_\pi$ transitions (open circles). There is no resonant enhancement for the $1s \rightarrow 4p_\sigma$ transitions.

It would seem natural to associate this absence with the incident polarization: With the incident polarization largely perpendicular to the CuO planes, there is significant coupling only with the $4p_\pi$ orbitals and no resonant enhancement is observed for the $1s \rightarrow 4p_\sigma$ transitions.

To test this idea, experiments were carried out in a vertical scattering geometry, with the incident polarization in the plane of the CuO sheets ($\epsilon \parallel ab$). A 6 eV feature was again observed when the incident energy was tuned through the Cu K-edge. The amplitude of the 6 eV excitation was extracted using the same procedure as outlined above and is also shown in the lower half of fig. 2 (closed circles) [9]. For this scattering geometry the resonance is at 9000 eV, i.e. it is associated with the $1s \rightarrow 4p_\sigma$ transitions. Since the only difference in the two experiments is the relative alignment of the incident polarization and the CuO sheets, we conclude that the incident polarization is indeed selecting the intermediate state of the resonance process.

In order to further explore the resonant scattering process, we have performed numerical calculations of the inelastic x-ray scattering, calculating the electronic structure of Nd_2CuO_4 within the Anderson impurity model and the scattering as a coherent second-order dipole process [10]. The parameter values used were the almost the same as in earlier work [10,11]. We discuss here the calculations have for the $1s \rightarrow 4p_\pi$ transitions, for which a Cu $4p_\pi$ band of width 2.0 eV is added to the model, together with an on-site Coulomb interaction $U_{pc} = 5.0$ eV (between the $4p_\pi$ and $1s$) and $U_{dp} = 3.0$ eV (between the $4p_\pi$ and $3d$).

In the CuO planes, the Cu $3d^9$ configuration hybridizes with $3d^{10}\underline{L}$, where $\underline{L}$ represents an O $2p$ ligand hole of finite bandwidth. Within the Anderson impurity model, this results in discrete bonding and anti-bonding states composed of a mixture of $3d^9$ and $3d^{10}\underline{L}$ configurations, with a continuous band between them (fig. 3). The ground state is then the bonding state, with about 60% $3d^9$. The lowest edge of the continuous band (charge transfer gap) is about 2eV above this and the anti-bonding state is $\sim$ 6 eV above the ground state.

In the intermediate state of the resonant scattering process, a Cu $1s$ electron is excited to the (for example) Cu $4p_\pi$ band, and the core hole potential reverses the balance between the $3d^9$ and $3d^{10}\underline{L}$ configurations. The lowest energy state is then predominately $\underline{1s}3d^{10}\underline{L}4p_\pi$ and is about 7 eV lower than the anti-bonding state, $\underline{1s}3d^9 4p_\pi$ (fig. 3). These states form the 8983 and 8990 eV features of the Cu K-edge XAS. (The $1s \rightarrow 4p_\sigma$ is similarly split.). Thus the resonant enhancement at 8990 eV is associated with the $\underline{1s}3d^9 4p_\pi$ intermediate state and that at 9000 eV with the $\underline{1s}3d^9 4p_\sigma$ intermediate state. Note no resonances are observed for the $\underline{1s}3d^{10}\underline{L}4p$ intermediate states.

Energy loss scans calculated for a number of incident energies are shown in fig. 4. For an incident energy of a 8990 eV, a single peak is observed at 6 eV, in agreement with the experimental data (c.f. fig. 1). The peak results from the decay of the intermediate state into the anti-bonding excited state. A single peak is observed because, for the $\underline{1s}3d^9 4p_\pi$ intermediate state, there is no significant overlap with the continuous band which is predominately $3d^{10}\underline{L}$, and decays into this band are therefore suppressed, so that only the discrete anti-bonding state is observed. As the incident photon energy is moved off resonance to 8987.5 eV, the intensity of the 6 eV feature drops, i.e the calculations correctly predict the resonant behavior of this excitation.

As the incident energy is lowered still further, to 8985 and 8983.5 eV, the calculated scattered intensity increases again, i.e. the calculations also predict a resonant enhancement associated with the $\underline{1s}3d^{10}\underline{L}4p_\pi$ intermediate state. As noted above however, no such resonance is observed in the experiments. Note that at this putative lower resonance, the calculated inelastic spectra exhibit a much broader feature, beginning at 2 eV, i.e. the continuous band and charge transfer gap are now observed.

One possible reason for the discrepancy between experiment and calculation at the lower resonance is the existence of solid state effects associated with the $\underline{1s}3d^{10}\underline{L}$ intermediate state. These arise because in Nd_2CuO_4 the CuO_4 plaquettes form an extended two dimensional network Such non-local effects are explicitly excluded from

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our calculations which were performed with the Anderson impurity model. As first pointed out by Veenendaal, Eskes and Sawatzky [12] such effects are most important for the well-screened intermediate states $3d^{10}\underline{L}$. The essential idea is that the $\underline{L}$ is repelled by the $\underline{1s}$ core-hole and moves onto another CuO_4 plaquette within the CuO plane. At this new site the copper is still in its ground state, i.e. largely $3d^9$, $S=\frac{1}{2}$ and the lowest energy state for *this* plaquette is to form a so-called Zhang-Rice (Z-R) singlet state with the $\underline{L}$ hole [13]. The energy gain in forming this singlet state helps stabilize the non-local screening.

While such ideas were first formulated in the context of photoemission experiments [12,14] for which the relevant core-hole was $\underline{2p}$, it seems likely that similar ideas hold for the intermediate state $\underline{1s}3d^{10}\underline{L}4p_\pi$. If this in fact correct and the intermediate state is a non-local excitation, then there will be little if any overlap with the 6 eV excitation since this latter state is strictly local and contains no Z-R singlet, even in extended clusters: The resonant enhancement is suppressed because of the small transition probability between states with and without Z-R singlets. Experiments to test these ideas by studying cuprates with different geometries for the connectivity of the CuO_4 plaquettes are currently underway. In addition, new calculations incorporating extended clusters which may be able to correctly represent the non-local effects are being performed. Preliminary results of both these efforts support our conclusions.

In summary, we have observed resonantly enhanced inelastic scattering from Nd_2CuO_4, with the incident photon energy tuned to the Cu K-edge. The excitation observed was of a charge transfer-type, involving the oxygen $2p$ and Cu $3d$ orbitals. Resonances associated with excitations into $4p_\sigma$ and $4p_\pi$ orbitals may be selectively excited by varying the relative orientation of the incident polarization and the copper oxide planes. The results broadly confirm recent cluster calculations for the CuO planes in high-T_C materials and suggest non-local effects play a role in controlling the resonance phenomena. Future experiments may provide sensitive, quantitative tests of such effects through measurements of resonant lineshapes and comparison with state-of-the-art electronic structure calculations.

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FIG. 1. Scattered intensity as a function of energy loss $(E_i - E_f)$ for a number of incident energies. Data are offset vertically for clarity and solid lines are guides to the eye.

FIG. 2 The amplitude of the 6 eV excitation, as a function of incident energy, for incident polarization largely perpendicular to the CuO planes (open circles) and parallel to the CuO planes (closed circles). The top half of the figure displays the absorption measured for powdered Nd_2CuO_4 (open circles), together with the theoretical absorption, as calculated using the same parameters as for the scattered intensity (fig. 4).

FIG. 3 Schematic energy level diagram for inelastic scattering from a copper site. Arrows indicate processes summed over in the calculation of the scattered intensity.

FIG. 4. Calculated energy loss scans for incident energies of 8990 eV (on resonance), 8987.5 eV, 8985 eV and 8983.5 eV. Note, the elastic scattering has been subtracted off.

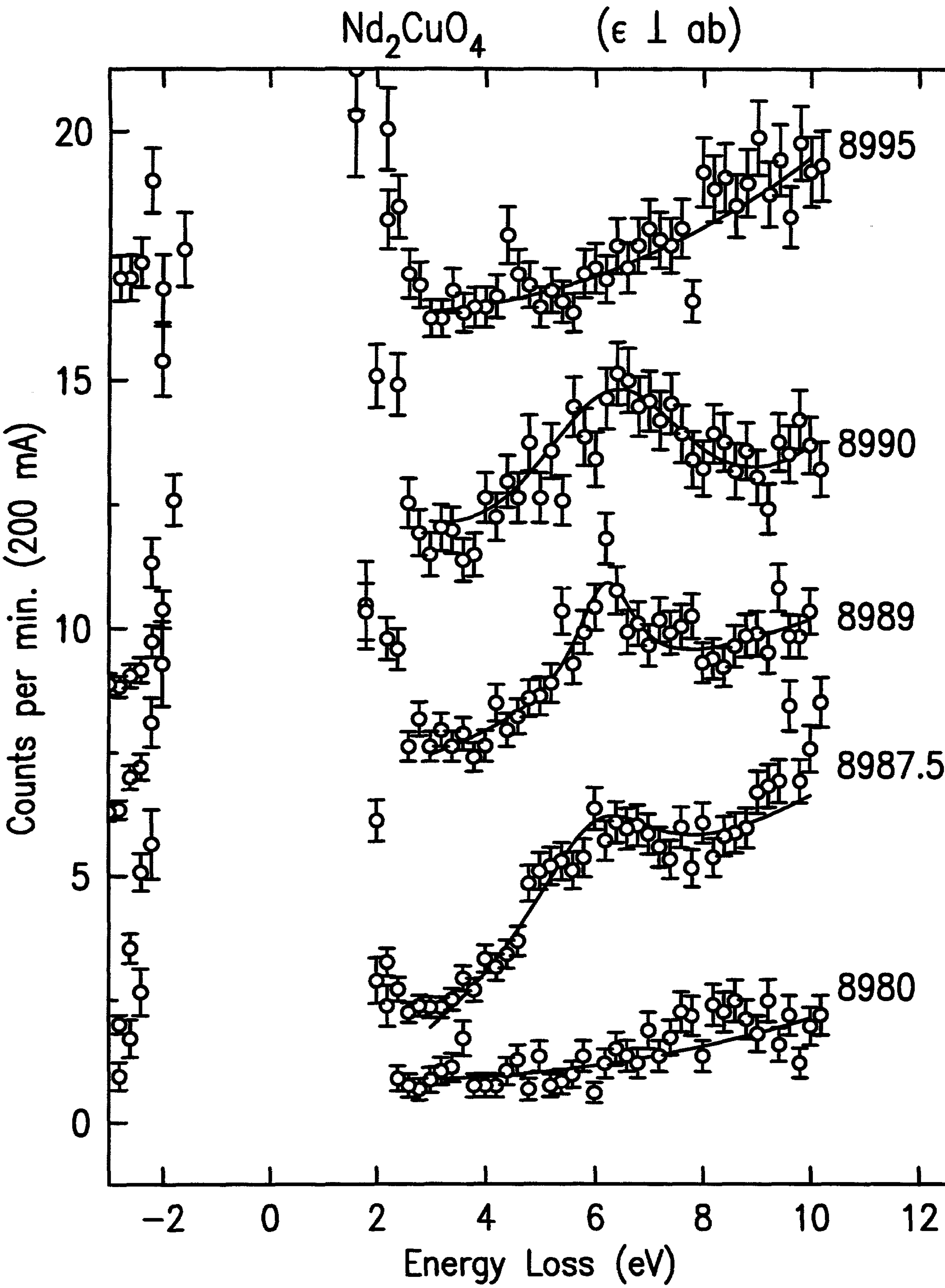

Fig. 1 Hill et al.

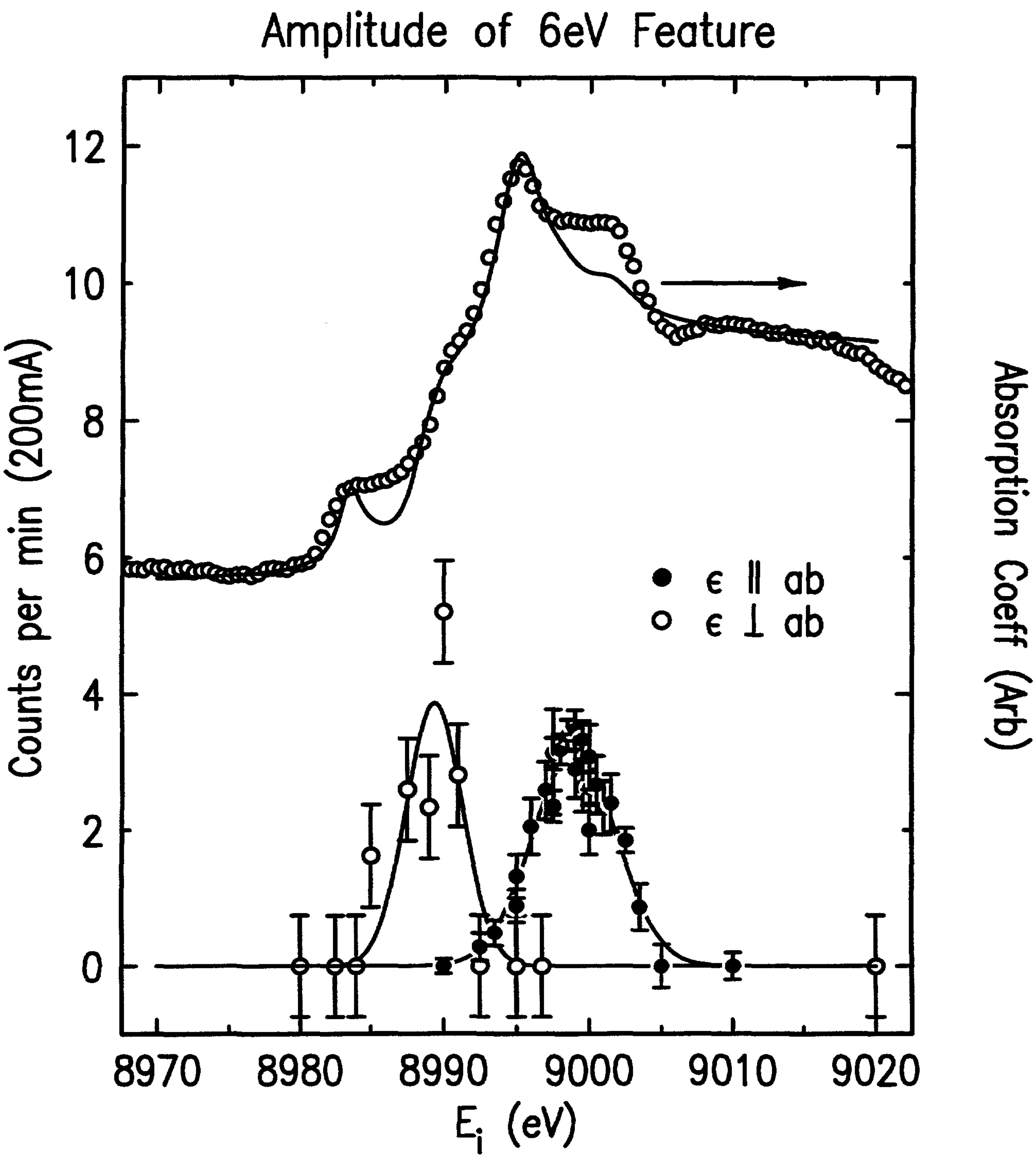

Fig. 2 Hill et al.

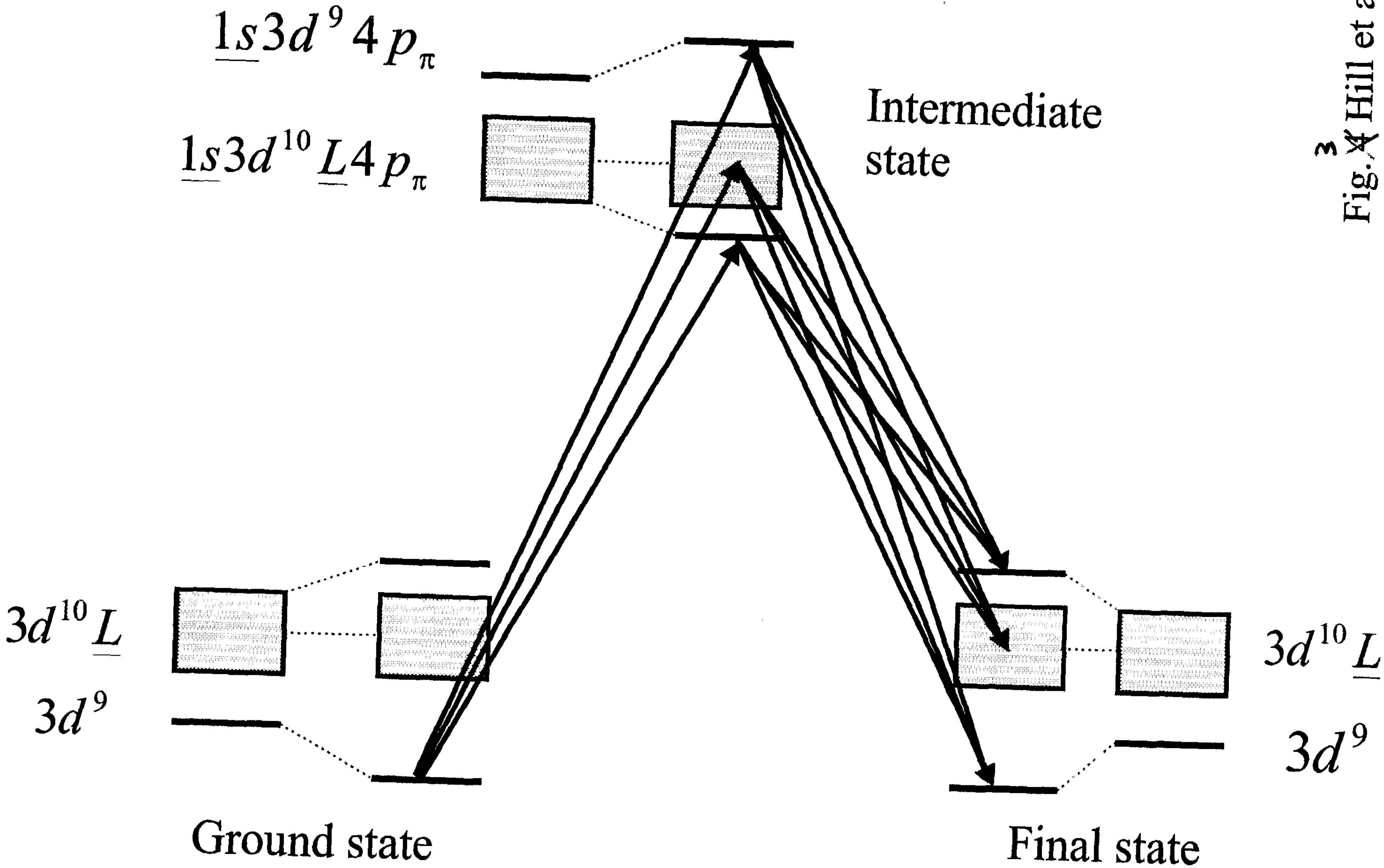

Fig. 3 Hill et al.

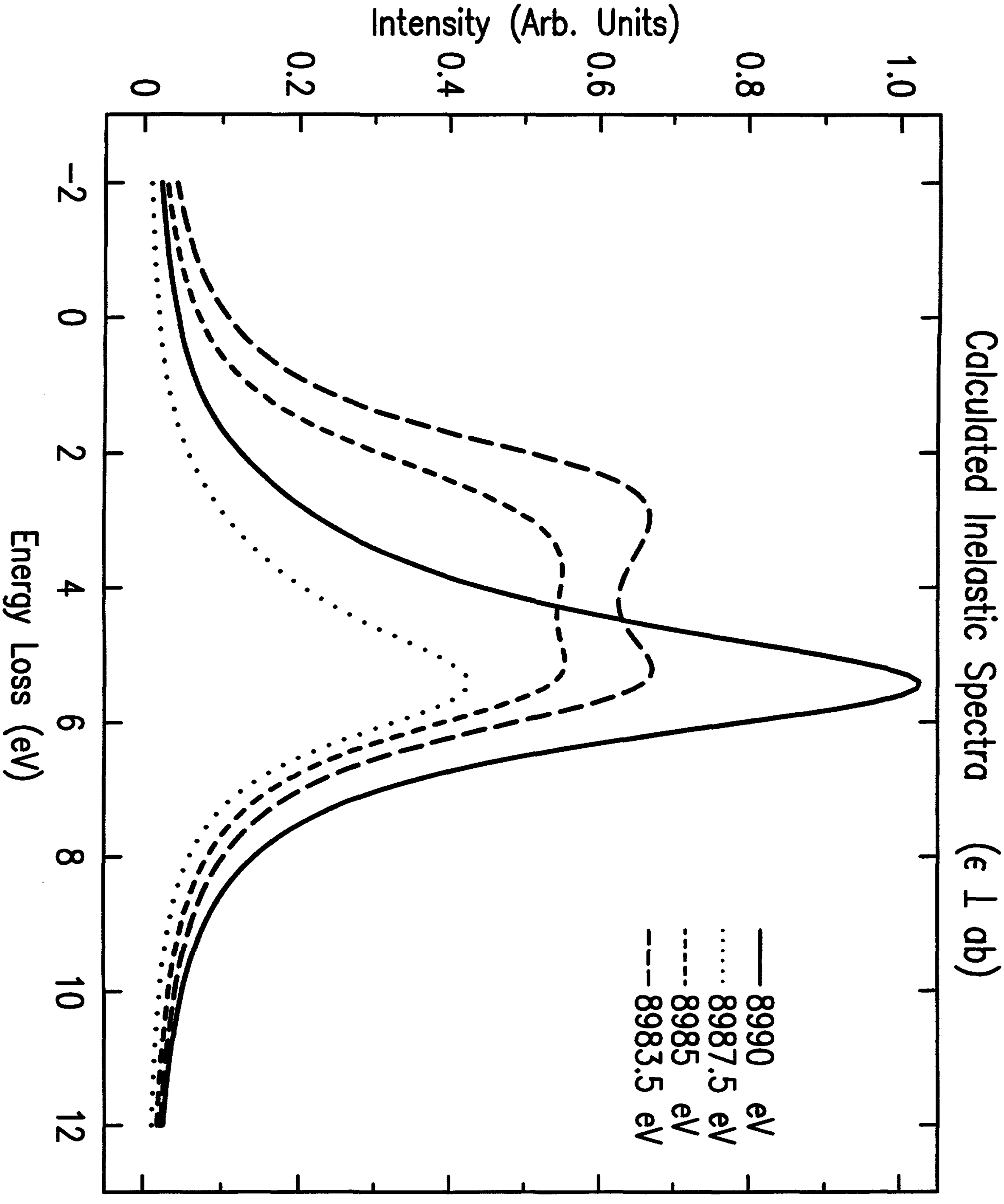

Fig. 4 Hill et al.