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Multielectron Contribution to Near-Edge X-Ray Absorption

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By comparison with photoelectron spectra which contain multielectron shakeup satellites, evidence is found for a structure in x-ray absorption near-edge spectra in $MnCl_2$, $FeCl_2$, and $CoCl_2$ produced by these same shakeup transitions. The strength of these shakeup satellites in absorption is weaker than in photoemission, as expected because of the different excitation energy of the photoelectrons involved.

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With the advent of synchrotron radiation sources, a rekindling of interest in measuring x-ray absorption spectra has occurred. The x-ray absorption spectrum is divided into near edge and extended fine structure. The extended x-ray absorption fine structure (EXAFS) covers the energy range from about 40 eV to about 1000 eV past the absorption edge, while the x-ray absorption near-edge structure (XANES) is the spectrum in the first 40 eV past the edge. Whereas the theory of the EXAFS is understood in general terms because it can be treated approximately by perturbation theory, XANES is more challenging theoretically because the potential must be treated to all orders.

One basic assumption almost universally made in calculating XANES is the single-particle picture where it is assumed that a single-particle density of states can explain the various peaks and valleys in the spectrum. This assumption has been strengthened by recent calculations[1-5] which appear to explain the positions of the measured features. Within the single-particle picture, some disagreement persists in whether the density of states of the initial solid[1-4] should be employed or the density of states of the final system with the excited core hole.[5-7] Recently, the validity of the single-particle picture for XANES has been questioned.[8,9]

Photoemission measurements in solids have revealed satellites besides the main peak. Many of these satellites have been shown to be caused by a multielectron excitation called a shakeup transition.[10] The shakeup transition is produced by the sudden creation of the core hole potential induced by the absorption of an x-ray photon. This sudden perturbation in potential knocks a "passive" electron into an excited state. "Passive" electrons are those not directly excited by the x-ray photon. When this state is a bound state the process is called a shakeup, and when this state is the continuum the process is called shakeoff. Shakeup processes can produce a sharp satellite while shakeoffs produce a smooth background. The photoelectron satellite then has a smaller energy than the main peak, because it had to share the photon energy with the excited shakeup electron. Thus, the difference in energy between the main peak and the satellite is the energy in the shakeup electron.

Such shakeup processes have been observed in the x-ray absorption spectrum of atoms[11-17] and in molecules.[17,18] The question naturally arises, why should such shakeup processes not be visible in the XANES of solids? In this Letter we show for the first time experimental evidence that they are visible. Figure 1 shows the photoelectron satellite structure observed[19] in exciting the $2p$ shell of Mn in crystalline $MnCl_2$. Note that the satellite is about 5 eV from the main peak. Ta-

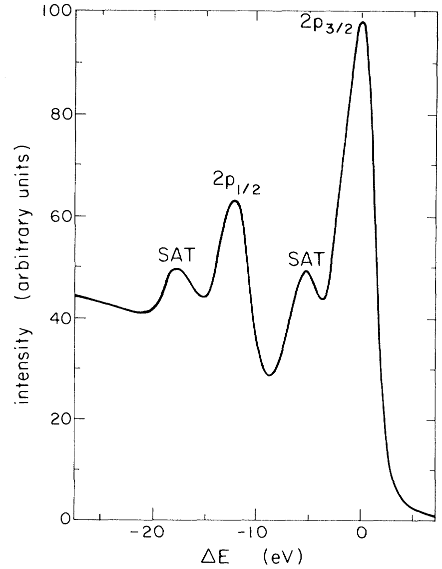

FIG. 1. Photoelectron spectra with Al $K\alpha$ x rays of the $2p$ shell of Mn in $MnCl_2$. The satellite structure is indicated by "SAT." Data are from Ref. 19.

TABLE I. Energy differences, ΔE, and relative intensities of satellites to main peak, I, from photoemission [denoted by the subscript one (from Ref. 19)] and x-ray absorption (denoted by the subscript two) experiments.

Material	ΔE_1 (eV)	ΔE_2 (eV)	I_1	I_2
$MnCl_2$	5.1	5.8± 0.3	0.38	0.041
$FeCl_2$	4.7	5.3± 0.4	0.48	0.077
$CoCl_2$	5.1	4.7± 0.4	0.70	0.16

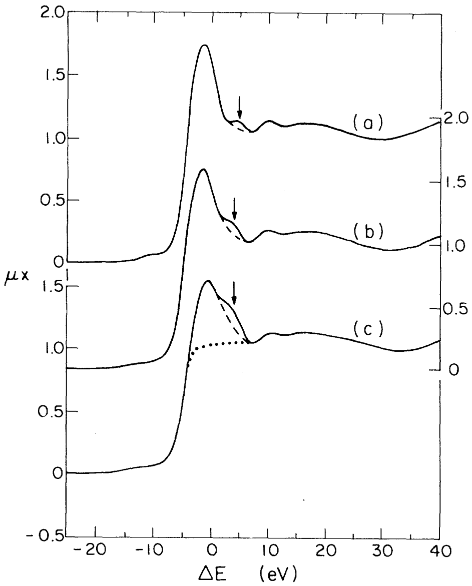

FIG. 2. The K-edge x-ray absorption spectra for (a) $MnCl_2$, (b) $FeCl_2$, and (c) $CoCl_2$. The satellite structure is indicated by the arrows and the assumed extrapolation of the first peak is indicated by the dashed lines. The dotted line in (c) is the assumed behavior of the edge if no first peak were present.

ble I lists the splitting between the satellite and the main peak, and the ratio of the peak height of the satellite to the main peak for $MnCl_2$, $FeCl_2$, and $CoCl_2$. The satellite structure in these cases has been shown convincingly to be due to a shakeup process.[19] X-ray absorption measurements on the same materials are shown in Fig. 2. The maximum of $\Delta\mu x$, the step in absorption coefficient times thickness, was below 1.2 in all samples, assuring no appreciable distortion due to the thickness effect.[20] A structure about 5 eV past the main peak grows in the same sequence as in the photoelectron spectra. The dashed lines in Fig. 2 are an extrapolation of the main peak. The dotted line in Fig. 2(c) is the assumed edge structure in the absence of the initial peak. Table I lists the ratio of the areas of the main and satellite peaks and their energy separation as measured by K-edge x-ray absorption. The location of the satellites in absorption agrees well within their width with the values found in photoemission, and the same trend in strength is seen in both cases. However, the absolute value of the ratio of the strengths is uniformly smaller in absorption. We will discuss below the large differences in strengths and the smaller variation of the energy of excitation. First, though, the case must be made to eliminate the possibility of explaining these structures by a single-particle density of states picture.

All of the three compounds studied here have the same crystal structure. Band calculations of the electronic band structure of these compounds[21] show very similar structure at the energies corresponding to the absorption peak of interest. In comparing the absorption structure with the band calculations it must be noted that the dipole selection rules select the p-symmetric portion of the density of states about the transition-metal atom. Thus the high density of unfilled d states produce a barely discernible rise in absorption starting about 10 eV below the main edge. The structure of interest is therefore about 15 eV above the Fermi energy. In this region of the band structure of the three compounds Ref. 21 states that "they are so similar . . . that it is useless to show them individually." The band calculations clearly cannot explain the large variation observed in the absorption feature of interest.

The similarity of the expected x-ray absorption features as predicted by band calculations is consistent with a systematic calculation of XANES for the K edges of the $4d$ transition metals[2] and the $3d$ transition metals.[3] The calculations show similar XANES for metals with similar crystal structure. Another single-particle effect that adds features in the x-ray absorption spectrum of molecules not present in that of atoms is the shape resonance.[22] However, this shape resonance effect, which is caused by a modification of the density of states due to the presence of the other atoms in the molecule, is automatically accounted for in band calculations in the case of solids and, as has been discussed above, cannot explain the feature of interest.

Since the properties of the absorption feature of interest cannot be explained by a single-particle picture, the connection with the multielectron excitation satellite of photoemission is strengthened. However, in order to complete the case for the similar origin of the satellite structure in photoemission and in absorption, the difference in the satellite strengths in the two cases must be explained. The difference is not caused by the different core hole excitations. In fact, the K-shell excitation should produce, if anything, a stronger satellite structure.[23,24] This difference is caused by the different excitation energy of the photoelectrons involved. In the photoemission results, Al $K\alpha$ radiation was employed, producing photoelectrons from the $2p$ shell of the transition metals with excitation energies of about 700 eV. In the x-ray absorption results, the excitation energy of the photoelectron that probes the satellite structure is at threshold. This difference in the energy of the photoelectron modifies the absorption strength in two ways. One is by the different shielding capability of the photoelectron. At the 700-eV excitation energy of photoemission, the photoelectron is in an energetic propagating state, and does not play a role in shielding the core hole. The shielding in this case occurs by a charge-transfer exchange between the Cl neighbors and the excited transition-metal atom. Since the transition-metal d states are more effective in shielding than the Cl p states, the excitations of the K-shell core hole transfers more transition-metal d character into the lowest-energy state of the excited system. This significant change in character of the "passive" electrons, after excitation, is the reason for a large strength to the shakeup transition as measured in photoemission. The larger the charge-transfer exchange, the greater the strength in the shakeup transition.[23]

In the x-ray absorption case, the photoelectron makes a transition to just above the Fermi energy, filling the empty levels composed of hybridized transition-metal d states and Cl p states. The photoelectron in this case partially shields the core hole from the Cl, and the charge-transfer exchange from the Cl neighbors is expected to be significantly weaker than in the photoemission case, weakening the shakeup transition as observed.

The shakeup electron also occupies the transition-metal d-state and Cl p-state hybridization levels and will have a significant interaction with the photoelectron in the absorption case. Such an interaction does not occur in photoemission, and the energy of the shakeup transition is not expected to be exactly the same in the two cases.

The absorption strength of the x ray also varies because of another cause as the energy of the photoelectron increases. This is observed experimentally[23] as an initially rapid increase of the strength of the absorption above threshold, reaching a saturation value when the photoelectron reaches kinetic energy several times the energy difference between the satellite and main peak. Qualitatively this variation has been explained[23] as the change from an approximate adiabatic turnon of the core hole potential at threshold to the sudden turnon of the potential at high photoelectron escape velocities. A more recent formulation of this problem[9] suggests that this turnon behavior of the x-ray absorption can be understood in terms of the photoelectron at threshold having more overlap with the initially occupied states than when it is energetic. This overlap introduces terms, called replacement terms by Friedel,[25] which suppress the absorption. In any case, the multielectron excitation picture is consistent with the experimentally observed facts in regard to the absorption feature of interest.

Finally, it is satisfying to note that the variation of the shape of the first absorption peak can also be understood in the multielectron picture. Referring to Fig. 1 it is noted that the first peak is narrowest for $MnCl_2$ and becomes broader and more asymmetric toward the high-energy side as the strength of the multielectron peak increases. The multielectron peak is caused by a shakeup to a discrete state. In addition to the shakeup processes, shakeoff excitation processes also occur[23] where the second excited electron ends in the continuum, producing an asymmetric broadening of the one-electron line shape.[26,27] The stronger the coupling to multielectron excitations, the larger the broadening.

In summary, evidence is given that multielectron shakeup effects contribute to the XANES of crystalline $MnCl_2$, $FeCl_2$, and $CoCl_2$. Caution should be exercised in relying on the currently employed assumption that a single-particle excitation spectrum can adequately explain XANES in all cases.

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Optically Induced Gap in the Atomic Tunneling Spectrum of As_2S_3 Glass

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Irradiation of the amorphous semiconductor As_2S_3 with band-edge photons opens a metastable gap in the low-energy density of states of atomic tunneling systems. Electric resonance studies at temperatures below 1 K indicate the annihilation of $\sim 10^{16}$ cm^{-3} tunneling centers, close to the density of metastable paramagnetic electronic defects created by low-level optical excitation. These findings link low-energy atomic tunneling systems to localized midgap electronic states.

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Low-energy tunneling systems dominate many of the properties of disordered solids at low temperatures.[1] Atomic tunneling between the two minima of a double-well potential results in two low-lying states with an energy splitting E. If the density of such two-level systems in glasses is approximately constant for energies <1 meV, the theory is in good agreement with the observed low-temperature properties. Nevertheless, a microscopic description of these centers has remained elusive.

It has often been suggested that there could be a connection between tunneling systems and electronic states in the gap of amorphous semiconductors, particularly the chalcogenide glasses.[2-8] However, wide disparities in the proposed densities of the two classes of defects as well as the different scale of excitation energies has made such an association rather tenuous. Irradiation with band-gap light forms electronic states which may be metastable at low temperatures, have an unpaired spin, and possess a broad optical absorption band in the gap.[9] The midgap absorption and spins can be removed by bleaching with light of an energy less than the band edge or by annealing above 150 K. These phenomena have been interpreted as the photoexcitation of charged defects to create neutral defects which have an energy near midgap.[3,10,11]

In this paper, we present the first experimental