Exchange-split Ca $3s^{-1}3d$ states in CaF$_2$ observed in threshold excited core-to-core fluorescence

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The Ca $2p^{-1} \rightarrow 3s^{-1}$ fluorescence transition in CaF$_2$ has been measured as a function of excitation energy in the threshold region of the $2p^{-1}3d$ absorption. The exchange splitting of the final Ca $3s^{-1}3d$ state, reached after populating intermediate atomiclike $2p^{-1}3d$ states, could be determined, together with the differential $3d$ electron screening, comparing a $2p$ and a $3s$ hole. It is demonstrated that the $2p_{1/2}^{-1}3d \rightarrow 2p_{3/2}^{-1}$ Coster-Kronig transition is energetically allowed, when the excited state is of t_{2g} symmetry. Additionally we obtain direct spectroscopic evidence that the $2p^{-1}3d$ states are populated in non-spin-conserving transitions ($\Delta S \neq 0$).

Multiplet splitting in ns level photoemission from an open-shell system arises from the final state exchange interaction between the valence electrons and the remaining ns electron.[1] For transition-metal compounds the $3s$ electron couples to incompletely filled d shells, giving rise to a double structure from which in principle conclusions about the $3s3d$ exchange interaction can be drawn. The quantitative evaluation is a theoretical challenge since these states are highly correlated. We here propose a method to study this interaction under the additional aspect of a modification of the occupancy of the $3d$ shell. This can be done in a soft x-ray absorption-emission process where in the first step a $2p$ electron is promoted to the $3d$ orbital and in the second step the excited electron stays as a spectator when a $3s$ electron fills the $2p$ hole, leaving the system in $3s^{-1}3d^{N+1}$ states. We demonstrate the method for the case of the Ca $3s$ hole in CaF$_2$. In this compound there are effectively no d electrons in the ground state, and we can accurately monitor the influence of a single d electron, added in the core excitation process.

With the development of bright synchrotron radiation sources it has become possible to study the excitation energy dependence of soft x-ray emission spectra. A rich phenomenology is encountered in the sub-keV region, where the impact of spectator vacancies as well as spectator electrons on the valence-band emission have been studied.[2-4] Interpretations of resonant phenomena in terms of inelastic scattering (resonant Raman scattering) have also been put forward.[2,5] Core-to-core transitions involve conceptually simpler excitations, and the interpretation is accordingly straightforward. The insight into the dynamics gained from such studies may help in the interpretation of the more complicated valence-to-core spectra. Moreover additional lifetime information can be obtained by analyzing the line shape of the fluorescence, which is difficult for valence-to-core transitions.

CaF$_2$ has been frequently studied because of its technical importance, mainly due to the ability to form high-quality interfaces with Si and GaAs. The $2p \rightarrow 3d$ absorption spectrum has been measured and discussed[6-8] and also the electronic decay of the excited states has been analyzed.[9] The present fluorescence spectra give in-

formation complementary to these studies. For the general analysis of the $2p$ excited states our data show directly that the $2p$ spin-orbit splitting exceeds the excitonic binding energy of the d electron in t_{2g} symmetry, leaving the $2p_{1/2}^{-1}3d \rightarrow 3p_{3/2}^{-1}$ Coster-Kronig (CK) channel open.

The experiment was carried out at the SGM monochromator at the X1B undulator beamline[10] at the NSLS in Brookhaven. The monochromatized beam from the movable output slit was refocussed onto the sample by means of a bendable float-glass mirror. The resolution of the incoming radiation was set to 0.6 eV. The fluorescence was analyzed in a recently constructed grazing incidence Rowland spectrometer. It is equipped with four interchangeable spherical gratings to cover the spectral range from 30 eV to above 1 keV with good resolution and efficiency. The gratings and a position-sensitive detector can be positioned and oriented along the various Rowland circles by means of computer-controlled x-y and rotational tables. Input slit length and width, as well as the acceptance of the spectrometer can be varied *in situ* to match the efficiency and revolving power. For the present data we used a 30 μm input slit and a 5 m grating with 1200 lines/mm, giving a resolution of around 0.5 eV in the first order. The spectrometer will be described in detail elsewhere.[11]

The sample was CaF$_2$ powder pressed into an indium foil. It is well known that synchrotron radiation induces fluorine desorption[12] and it has been shown that electron yield (EY) spectra exhibit changes after exposure to white light.[8] After 0.5 h exposure to the intense monochromatic radiation from the X1B beamline we notice small changes in the EY spectra (see Fig. 1). Even though these changes probably are insignificant for the much more bulk-sensitive fluorescence measurement, we took care in always measuring on previously unexposed spots for less than 30 min.

The Ca L EY spectrum of CaF$_2$ shown in Fig. 1 is very similar to previously published spectra.[6] The spectrum has been successfully interpreted on the basis of model calculations for a Ca^{2+} ion in a ligand field, using parameters for spin-orbit coupling, p-d Coulomb and exchange interaction, and for the crystal-field splitting.[7,8] The localized nature of the excitations has also been demon-
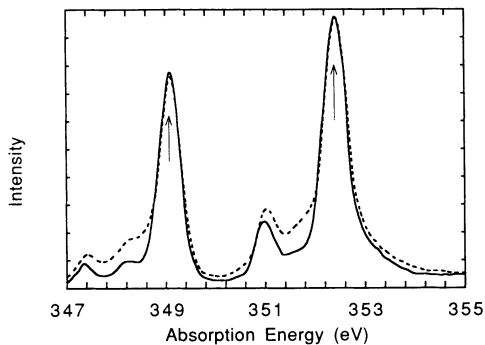
FIG. 1. Ca L electron yield spectra of CaF_2, before (solid line) and after 0.5 h exposure (dashed line) to monochromatized synchrotron radiation at 352.4 eV. The two arrows indicate the excitation energies for the fluorescence spectra shown in Fig. 2.

strated in the dramatic excitation energy dependence of the electronic decay.[9]

The resonant behavior of the Ca L x-ray fluorescence excited in the threshold region is shown in Fig. 2. The excitation energies are as indicated in Fig. 1 at 357.6 eV, above threshold (bottom), and at the two most intense peaks in the absorption spectrum at 352.4 eV (center) and 349.1 eV (top).

The high-energy excited spectrum shows two peaks, at 302 eV and 305.5 eV. In the spectrum excited at 352.4 eV the low-energy peak is less intense and the high-energy peak is shifted towards lower transition energies and split into a double structure. At the lowest excitation energy we observe one double-structured peak shifted towards lower energies relative to the low-energy peak in the previous spectra.

A proper theoretical treatment of the excitations and especially the final 3s hole states has to include correlation. For the Ca atom it has been shown that the state dominated by the $3s^{-1}$ configuration is considerably mixed with other configurations, and we are faced with a breakdown of the one-electron picture.[13,14] We show below, however, that the one-electron picture can be used

to qualitatively understand our spectra, and that useful information can be extracted on this level of approximation.

In Fig. 3 we show a schematic energy diagram where the transitions corresponding to the peaks in Fig. 2 are labeled. The two peaks in the spectrum excited above threshold are assigned to transitions from the two initial spin-orbit split 2p hole states to the same final 3s hole state. The energy separation of the two emission lines reflects the energy separation between the initial states $(2p_{1/2}^{-1}, 2p_{3/2}^{-1})$. The peaks are to a good approximation Lorentzians with a full width at half maximum of 1.3 eV. It is tempting to interpret this as the lifetime width of the final state. This would imply a surprisingly short lifetime, considering that the $3s3p^6 \rightarrow 3s^23p^4$ CK decay is energetically forbidden. The dominating decay channels must involve at least one of the valence electrons, which are mainly of $F\ 2p$ character.

We now turn our attention to the spectrum excited on the low-energy absorption peak (Fig. 2 top curve). In the simplest approximation one can regard the initial state as a $2p_{3/2}$ hole with an excited 3d electron. The x-ray transition would then leave the system in the $3s^{-1}3d$ state. In this picture the difference between this transition and the one assigned to the low-energy peak in the spectrum excited above threshold is the presence of a spectator 3d electron in the initial and final states of the transition.

This 3d electron shifts the emission structure to lower emission energy. This can readily be understood as differential Coulomb screening of the core holes in the initial and final states. The Coulomb interaction between the 3d electron and the 2p hole is larger than between the 3d electron and the 3s hole, making the binding energy of the 3d electron larger in the initial state than in the final state of the x-ray transition.

We interpret the splitting of the peak as the exchange splitting of the $3s^{-1}3d$ final state. In the one-electron picture this splitting is[1]

$$\Delta E = (2S + 1)K_{3s,3d}\ ,$$

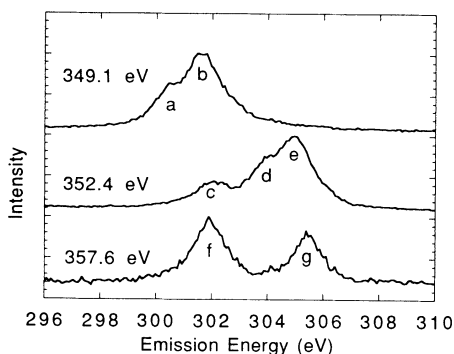## Core-to-Core Transitions in CaF_2

FIG. 2. Soft x-ray fluorescence spectra excited at 349.1 eV (top), 352.4 eV (middle), and 357.6 eV (bottom). The peaks are assigned to the transitions indicated in Fig. 3 as labeled. The absolute energy scale is determined from photoemission data and can be slightly in error due to phonon relaxation. This does not affect our discussion.
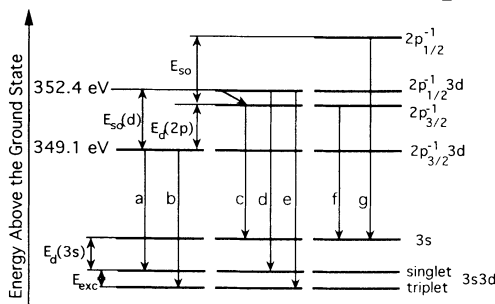

FIG. 3. Schematic energy scheme indicating the relevant levels and transitions. The arrows are labeled as the peaks in Fig. 2. Our results show that $E_{so}(d) > E_d(2p) > E_d(3s)$, where $E_{so}(d)$ is the spin-orbit splitting of the 3d (t_{2g}) excited state, and $E_d(2p)$ and $E_d(3s)$ are the excitonic binding energies of the 3d electron in the 2p and the 3s excited states, respectively. We determine the exchange splitting of the $3s^{-1}3d$ state, E_{exc}, to be 1.3 eV.

where $K_{3s,3d}$ is the exchange integral and $S = \frac{1}{2}$ in the case of a triplet-singlet splitting. We do not expect this equation to predict the splitting quantitatively correct. It is known to give slightly erroneous values for transition-metal compounds due to correlation effects,[1] and, as mentioned above, correlation must be important in the final $3s^{-1}3d$ states. An atomic calculation for a Ca^{2+} ion, based on the density functional theory in the local spin density approximation,[15] that includes exchange and correlation from the homogeneous electron gas predicts the splitting to be 0.9 eV,[16] close to the experimental splitting of 1.3 eV.

The observation of transitions to the triplet state (the intensity is even higher than for the transition to the singlet state), implies that the spin is not conserved in the absorption-emission transitions. This shows that the LS coupling scheme is inappropriate for at least one of the involved states. In the $2p^{-1}3d$ intermediate state the spin-orbit coupling is comparable to the Coulomb interaction, and as we will show below it is even larger. Hence, for the intermediate state the LS coupling scheme must be invalid. This is confirmed by model calculations of the absorption spectrum that have been carried out in a jj-coupling scheme.[7,8] Here the excited states are described as linear combinations of triplets and singlets. In the final $3s^{-1}3d$ states, on the other hand, the spin-orbit coupling is small and it is again legitimate to assign well-defined spins to the states.

The spectrum excited at 352.4 eV exhibits a similar double structure as the spectrum discussed above. The structure is shifted to higher energies with the excitation energy, and it is straightforward to assign this structure to transitions from a $2p_{1/2}^{-1}3d$ initial state to the same exchange split $3s^{-1}3d$ final states as above (see Fig. 3).

The additional low-energy peak at 301.9 eV coincides with the low-energy peak in the spectrum excited above threshold, and we therefore assign it to the same $2p_{3/2}^{-1} \rightarrow 3s^{-1}$ transition. The observation of this transition can be taken as direct proof that the energy of the $2p_{1/2}^{-1}3d$ state lies above the $2p_{3/2}$ ionization limit. In other words, the spin-orbit splitting of the $2p^{-1}3d$ states exceeds the excitonic binding energy of the $3d$ electron, as is shown in Fig. 3. The former is directly determined from the absorption spectrum to be 3.3 eV, whereas the latter has been determined by combining optical and photoemission data to be 3.7 eV.[9] This obviously contradicts our present results.

When comparing data from different spectroscopies one has to be aware of phonon relaxation. For some insulators it has been found that the magnitude of phonon relaxation shifts is on the order of 1 eV,[17] and also that core-ionized states tend to relax more than core-excited excitonic states. Such an effect could explain a reverse ordering of the two excited states in emission and absorp-

tion spectroscopy.

The analysis of the absorption spectrum indicates that the cross section for direct $2p_{3/2}^{-1}$ ionization is negligible at the excitation energy of 352.4 eV. Therefore the ionic state must be populated primarily via the CK decay, as is indicated in Fig. 3. The above discussion suggests that this decay process is assisted by vibrational excitations. From the relative intensity of the 301.9 eV feature to the main line we see that the probability for CK decay is small compared with the probability for decay in competing channels. We will discuss the relative decay rates in more detail in a forthcoming publication.

We note again that the final states have well-defined spin alignment. Since long-range magnetic ordering can be ruled out in the otherwise closed-shell electronic structure of CaF_2, we can regard the triplet excitations as locally inducing paramagnetism over the lifetime of the states ($\tau < 10^{-15}$ s).

The strong correlation has so far hampered a first principles description of the core excitations in CaF_2. As mentioned above the Ca L absorption spectrum has only been treated using a model Hamiltonian with fitted parameters.[7,8] We hope that this type of measurement will add information that is useful for the understanding of such a highly correlated system. In a first application our data can serve as a consistency check of the parameter set used to describe the core excitations, imposing the constraint that the absorption and the decay must be described by the same parameters.

In conclusion, threshold-excited soft x-ray fluorescence populates states otherwise difficult to access. In particular it can be used to measure the $3s3d$ exchange interaction in $3d$ compounds with the option of modifying the $3d$ occupancy. We measured the Ca $3s3d$ exchange interaction in CaF_2, which has a nonmagnetic closed-shell ground state. It was shown that the $3d$ Coulomb screening of the $3s$ hole is smaller than that of the $2p$ hole. This type of measurement also gives important information about the excitation-emission dynamics. We showed that the $2p_{1/2}^{-1}3d$ state can decay to the ionic $2p_{3/2}^{-1}$ state, and that the excitonic states have to be described in intermediate coupling which specifically leads to spin-flip transitions. Here we have discussed only the most intense $3d$ excitations of t_{2g} symmetry. Complementary studies involving also the other excitations are under way.

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