Enhanced Multielectron Effects in the Core-Level Spectra of Calcium, Strontium, and Barium

L. Ley, N. Mårtensson,[a] and J. Azoulay[b]

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 29 February 1980)

Intrinsic collective losses are observed in the core-level spectra of Ca, Sr, and Ba that exceed those observed in Al, Mg, and Na by factors up to 10. The coupling strength depends on the nature of the core hole. The relationship between the strength of the collective excitations and the extraatomic relaxation energies explains increases of 1.0 eV and 0.3 eV in Ca $3p$ and Sr $3p$ splittings compared to the free-ion spin-orbit splittings.

The many-body aspect of the photoemission process finds its experimental manifestation in two observations[1,2]: the relaxation energy and the occurrence of satellites. The binding energy of a core level is smaller than the Koopmans-theorem value E_K calculated for a strictly one-electron transition by the relaxation energy E_R. The origin of E_R is the lowering of the final-state energy when the "passive" orbitals are allowed to rearrange in accordance with the increased positive charge due to the missing electron. A number of weaker structures towards lower kinetic (higher binding) energy are usually observed which reflect transitions leaving the system in final states different from the fully relaxed quasi-ground state. Thus a correct description of the photoemission process requires a full many-body treatment which yields a spectral distribution $A(\omega)$ of final states.

A sum rule, first proposed by Lundquist,[3] relates $A(\omega)$ to the energy of the Koopmans-theorem value E_K and the energies E_B and E_R according to

$$\int (d\omega/2\pi)[\omega A(\omega)] = E_K = E_B - E_R. \tag{1}$$

Expression (1) states that the weighted average of the spectral distribution is at the position of the frozen orbital binding energy. We expect that for a high intensity of satellites E_R is large, all other parameters being equal.

In addition to the "intrinsic" satellites just mentioned extrinsic losses suffered by the photoelectron on its way through the solid contribute to the spectrum. The separation of these two species have been the central problem in studying multielectron effects of this kind in solids.[4-7] For simple metals the satellites are plasmons and intrinsic plasmon contributions between 10% and 44% have been measured in the most studied metals Al, Mg, and Na.[6,7]

In this Letter we report intrinsic losses in Ca, Ba, and Sr that *exceed* the extrinsic ones by fac-

tors up to 10. The structure of these losses follows closely, in all cases, the loss function $\text{Im}(-1/\epsilon)$. They thus represent excitations that are characteristic for the metal rather than the atom. Their high intensity makes it possible to observe further differences in the coupling strength of the excitations depending on the quantum numbers of the core hole. In particular, an increase of the apparent Ca $3p$ spin-orbit splitting by more than 1 eV over the free-ion value is traced to such a difference and the accompanying variation in relaxation energy.

The x-ray–excited core-level spectra [x-ray photoemission spectroscopy (XPS)] of Ca, Sr, and Ba were measured in a Hewlett-Packard Model-5950A ESCA spectrometer with use of monochromatized Al $K\alpha$ radiation in a vacuum of 6×10^{-11} Torr. The resolution obtained was 0.7 eV. The metals were measured as films evaporated onto polished stainless-steel substrates.

In Fig. 1 we have plotted the spectra of those core levels that could be recorded over a range of 20 eV without interfering emission from other lines. The second spin-orbit component ($p_{1/2}$, $d_{3/2}$) was removed with use of a stripping procedure. Starting with the background at low binding energies, a reduced replica of the original spectrum shifted by the spin-orbit splitting was subtracted from the spectrum channel by channel proceeding towards higher binding energies. All deconvolutions were made with the statistical intensity ratio and the spin-orbit splittings used were Ca $2p$ (3.74 eV), Ca $3p$ (1.40 eV), Sr $3p$ (10.33 eV), Sr $3d$ (1.74 eV), Sr $4p$ (1.30 eV), Ba $4d$ (2.63 eV), and Ba $5p$ (2.19 eV). Some spectra are broadened by Lorentzians of adjustable width in order to account for the different core-hole lifetimes and to equalize the widths of all main lines at 2 eV full width at half maximum (FWHM). For the broad Sr $3p_{3/2}$ line a Lorentzian contribution of 1 eV was deconvoluted to obtain a width of
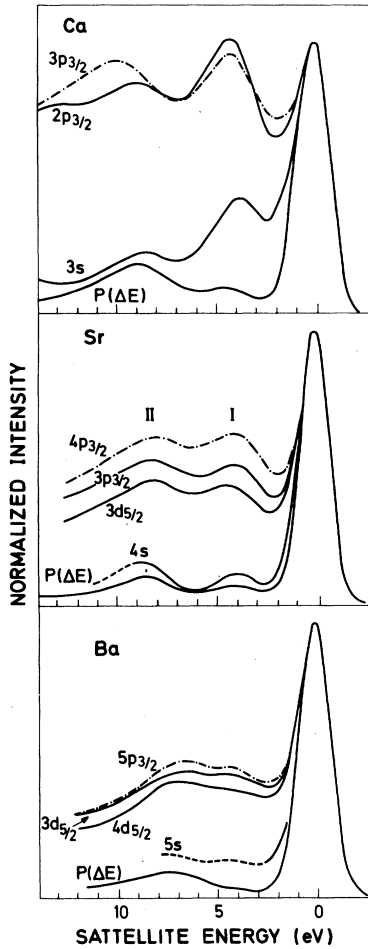

FIG. 1. Normalized core-level spectra of Ca, Sr, and Ba. The dashed portion of the Ba 5s spectrum has been corrected for contributions from the 5p losses.

2 eV. In this way all spectra are directly comparable in intensity and shape. Also shown in Fig. 1 are the distributions of extrinsic losses $P(\Delta E)$. They are calculated along the lines described by Penn[6] utilizing the loss function $\text{Im}[-1/\epsilon(\Delta E, q)]$ as measured by Langkowski,[8] where $\epsilon(\Delta E, q)$ is the energy (ΔE) and momentum-$(q$-) dependent dielectric function. Since loss processes with all q vectors contribute to $P(\Delta E)$ an integration over q was performed with use of the formula given by Raether[9] for the q-vector-dependent differential scattering cross section. The dispersion and damping of the losses contributing to $\text{Im}[-1/\epsilon(\Delta E, q)]$ as a function of q were taken into account through the parameters given by Langkowski. The intensity of $P(\Delta E)$ is deter-

mined by the relationship[10]

$$\int_0^{\Delta E} \text{max} P(\Delta E, E_0) d\Delta E = 0.9 I(E_0).\qquad(2)$$

$I(E_0)$ is the intensity of the no-loss line with a kinetic energy E_0. The integral is calculated to a certain energy $\Delta E_{\max}$, in our case 60 eV. Up to this energy, $\text{Im}[-1/\epsilon(\Delta E, q)]$ was known. The factor 0.9 accounts for contributions to the loss probability with energies greater than $E_{\max}$.[11] $P(\Delta E, E_0)$ is also a function of E_0. However, the shape of $P(\Delta E)$ depends so little on E_0 for E_0 between 800 and 1400 eV that we have plotted $P(\Delta E)$ only for $E_0 = 1100$ eV. Surface plasmons are not included in $P(\Delta E)$. They are generally weak[6] except in Ca where they could account for some of the difference between $P(\Delta E)$ and the 3s spectrum in the region around 4 eV (see Fig. 1).

We are now in a position to make the following observations:

(i) All but outermost s core levels exhibit satellite structures that exceed the intrinsic losses in amplitude by a factor between 6 and 10 for Ca, between 4 and 6 for Sr, and by about a factor of 5 for Ba. These intensities exceed by far the strength of the intrinsic losses observed in Al, Mg, and Na which are in agreement with the estimated coupling strength for intrinsic plasmon losses of approximately $r_s/6$, where r_s is the radius of a sphere containing one electron. Since the r_s values for Ca, Sr, and Ba fall in the range spanned by the aforementioned metals, we would expect similar intensities in these cases if they followed the $r_s/6$ rule.

(ii) The ranges of relative amplitudes given above hold for most core levels; a noticeable exception are the outermost s core levels. Their satellite intensities follow approximately the $r_s/6$ rule, i.e., the intrinsic loss intensity amounts to about 40% to 50% of the total loss intensity.

(iii) The structure of the loss spectra resembles closely that given by the loss function $\text{Im}(-1/\epsilon)$. This holds also for a broad maximum in the loss function around 30 eV which is not shown in Fig. 1. The shift of satellite II in the Ca $3p_{3/2}$ spectrum results most probably from an unresolved double loss that is resolved at 13 eV in the Ca $2p_{3/2}$ spectrum. We take this similarity between $\text{Im}(-1/\epsilon)$ and the observed satellite spectrum as evidence that the excitations which couple so strongly to the core holes are collective in nature in the sense that they are characteristic for the metal and not for the atom.

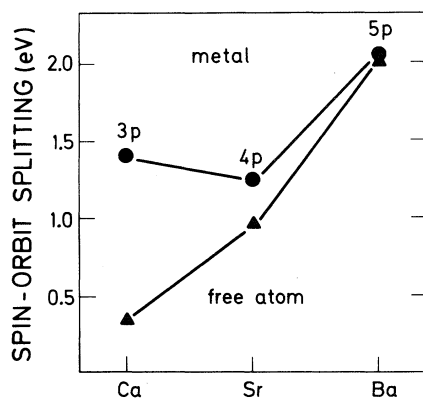In Fig. 2, we compare the separations between the outermost p core levels in the metal with the

1517

FIG. 2. Splitting of the outermost p levels for the free ion of Ca, Sr, and Ba and for the corresponding metals.
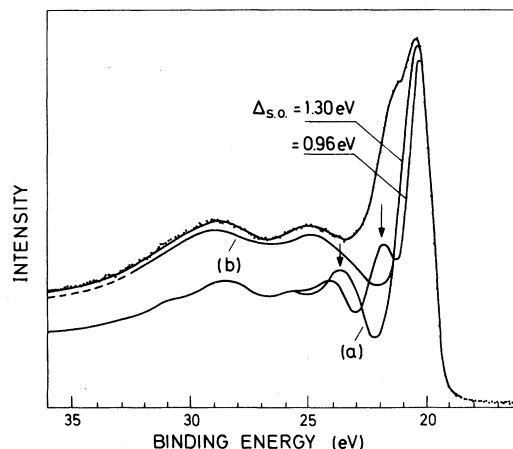

FIG. 3. The Sr $4p_{3/2}$ spectrum after subtraction of the $4p_{1/2}$ spectrum assuming different separations between the two levels and different satellite intensities. The dots represent the original spectrum.

corresponding spin-orbit splittings in the free ion.[12] We find an excess splitting in the metals of 1.06 eV for Ca, 0.34 eV for Sr, and about 0.05 eV for Ba. These deviations are so strong that they result in a *smaller* apparent spin-orbit splitting for Sr than for Ca in contrast to the expected monotonic *increase* with atomic number.

Small increases (+0.1 to + 0.3 eV) in the spin-orbit splitting compared to the free-atom values have been observed earlier in a number of metal d levels.[13] In this context possible reasons for these deviations have been discussed. They could all be dismissed except for a crystal-field or band-structure effect on the rather loosely bound ($E_B \simeq 10$ eV) d levels.[13,14] Such an explanation is impossible in the present case: The binding energies of the outermost p levels are ~ 25 eV for Ca, ~ 21 eV for Sr, and ~ 15 eV for Ba. Thus the level with the highest binding energy shows the greatest increase in the apparent spin-orbit splitting which rules band-structure effects out as an explanation.

We have made attempts to fit our spectra to two lines separated by the free-ion spin-orbit splitting. Figure 3 shows as an example the original data of the Sr $4p$ lines and three spectra obtained after removing the $4p_{1/2}$ component through the stripping procedure. If we adopt the free-ion spin-orbit splitting[12] of 0.96 eV a residual peak 1.4 eV below the main line remains that cannot be removed by varying the intensity of the width of the $4p_{1/2}$ component. If we require the $4p$ splitting to be 0.96 eV, we would have to explain this low-lying satellite which occurs only on the $4p_{3/2}$ line in Sr and a corresponding satellite on the Ca $3p_{3/2}$ line. Explanations involving chemical

shifts due to contaminations or surface species must be ruled out because they require similar satellites on all other core levels. We are thus left with an as yet unknown but highly selective new excitation mechanism as an explanation for this satellite.

Alternatively we would like to propose a different explanation for the increased p-level splitting that is based on the relationship between relaxation energy and the intensity of the intrinsic loss spectrum alluded to above. Taking again Sr as an example (Fig. 3), we find that the $4p$ spectrum can be fitted if we assume a spin-orbit splitting of 1.30 eV *and* a satellite spectrum that is reduced to that of the $4s$ level (curve b of Fig. 3). If this reduction is disregarded, a low-lying satellite appears (curve a of Fig. 3) which would have to be explained. We can now invoke the sum rule (1) as an explanation for the increased $4p_{1/2}$-$4p_{3/2}$ splitting: The initial-state splitting is 0.96 eV as observed in the free atom. In the solid the relaxation of the $4p_{3/2}$ is larger than that of the $4p_{1/2}$ level due to due to different coupling strengths of the two levels to the excitation spectrum of the metal. The same arguments hold for the p levels of Ca and Ba.

While this explanation is admittedly still speculative it finds support by three additional observations.

(i) The difference in relaxation depends on the overall strength of the satellite spectrum which decreases from Ca over Sr to Ba as does the increase in the $p_{1/2}$-$p_{3/2}$ splitting.
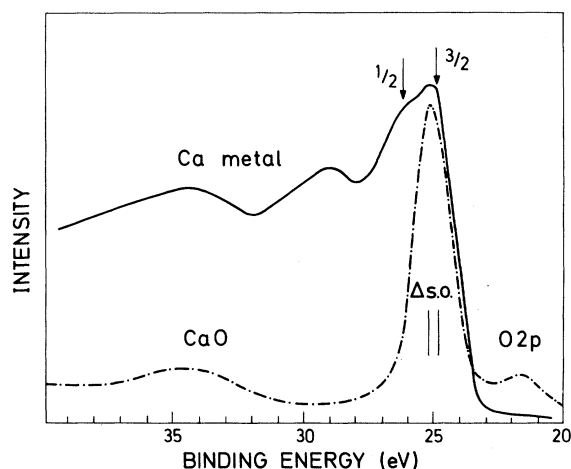
FIG. 4. The Ca $3p$ spectrum in Ca metal and in CaO. The spectra have been aligned.

(ii) As a consequence of the unusually high coupling strength of the core holes to the excitation spectrum of these metals we would expect very high *extra-atomic* relaxation energies. The extra-atomic relaxation energies of Ca, Sr, and Ba are indeed only surpassed by those of Li according to a recent study by Johansson and Mårtensson[15] if one disregards the transition metals.

(iii) A reduction in the coupling strength should result in a reduction of the apparent spin-orbit splitting. This is indeed observed if we compare the $3p$ spectrum of Ca with that of CaO in Fig. 4. The single line in CaO is expected for an unre-

solved spin-orbit splitting of 0.35 eV.

(a)Permanent address: University of Uppsala, Uppsala, Sweden.

(b)Permanent address: The Hebrew University, Jerusalem, Israel.

[1]See, e.g., D. A. Shirley, in *Topics in Applied Physics*, edited by M. Cardona and L. Ley (Springer, Berlin, 1978), Vol. 26, p. 165.

[2]J. W. Gadzuk, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, Chichester, N. Y., 1978), p. 111.

[3]B. I. Lundquist, Phys. Kondens. Mater. 6, 167 (1967).

[4]D. C. Langreth, in *Collective Properties of Physical Systems*, edited by B. Lundquist and S. Lundquist (Academic, New York, 1974), p. 210.

[5]W. J. Pardee, G. D. Mahan, D. E. Eastman, R. A. Pollak, L. Ley, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 11, 3614 (1975).

[6]D. R. Penn, Phys. Rev. Lett. 38, 1429 (1977).

[7]P. Steiner, H. Höchst, and S. Hüfner, Z. Phys. B 30, 129 (1978).

[8]J. Langkowski, J. Phys. D 8, 2058 (1975).

[9]H. Raether, in *Springer Tracts in Modern Physics*, edited by G. Höhler (Springer, Berlin, 1965), Vol. 38, p. 84.

[10]P. A. Wolff, Phys. Rev. 95, 56 (1954).

[11]C. Powell, Surf. Sci. 44, 29 (1974).

[12]W. Schmitz, B. Brenckmann, and W. Mehlhorn, J. Phys. B 9, L493 (1976); W. Mehlhorn, B. Brenckmann, and D. Hausmann, Phys. Scr. 16, 177 (1977).

[13]L. Ley, S. P. Kowalczyk, F. R. McFeely, and D. A. Shirley, Phys. Rev. B 10, 4881 (1974).

[14]N. Shevchik, J. Tejeda, M. Cardona, and D. W. Langer, Phys. Status Solidi (b) 59, 87 (1973).

[15]B. Johansson and N. Mårtensson, private communication.

Surface-Enchanced Raman Scattering from Pyridine on Ag(111)

P. N. Sanda, J. M. Warlaumont, J. E. Demuth, J. C. Tsang, K. Christmann,(a) and J. A. Bradley

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

This Letter reports the first ultrahigh-vacuum study of surface-enhanced Raman scattering from pyridine adsorbed on a clean single-crystal silver surface containing a smooth modulation (1 μm periodicity) to allow optical coupling to surface plasmon polaritons. A large mode-selective enhancement ($\sim 10^4$) of the Raman signal from the first monolayer is observed at surface-plasmon-polariton resonance. Coverages greater than one monolayer show a smaller enhancement ($\sim 10^2$).

PACS numbers: 78.30.Jw

Surface-enhanced Raman scattering has been observed in electrochemical cell systems,[1] tunnel-junction structures,[2,3] discontinuous films,[4] small particles in solution,[5] and recently for surfaces prepared in ultrahigh vacuum (UHV).[6-8] Recent UHV experiments have used the photoreac-