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Resonant Photoemission in Barium and Cerium

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In this Letter, a theoretical discussion of resonant photoemission in barium and cerium is presented. Calculations are performed using a time-dependent density-functional technique which both is accurate and provides a simple physical interpretation of the resonant phenomena.

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Recent experiments using synchrotron radiation have revealed giant enhancements in the valence-level photoemission from rare-earth metals and compounds which are associated with the large broad maximum observed in photoabsorption above the $4d$-ionization threshold.[1,2] For example, the resonant $4f$ emission is now being used as a "fingerprint" technique to study valence changes in these interesting materials.[3,4] In this work we report the first calculations which exhibit this resonant $4f$ emission in cerium and illustrate how this effect is common to all the valence levels. In addition, we show that a close connection exists between this and similar behavior observed in the well-studied case of barium photoemission.[5-7] An important aspect of our work is that all the above-mentioned phenomena may be very simply understood within the "local field" framework of our theoretical methods.

Our calculations are based upon a generalization of the Hohenberg-Kohn-Sham density-functional formalism[8] recently introduced in a study of rare gas photoabsorption.[9] The method is essentially a time-dependent local density approximation (TDLDA) in which the external radiation field is replaced by an effective local field, $\varphi^{\mathrm{SCF}}(\vec{r},\omega)$, which self-consistently takes account of the response of the electronic charge density to the external perturbation. Since the total photoabsorption in the vapor and that in the condensed phase are practically identical for both barium and cerium in the photon energy range of interest,[10,11] we have performed all of our calculations for the case of the free atom.

In the manner of a typical self-consistent field theory, the complex frequency-dependent local field is related to the Fourier components of the time-dependent density disturbance $\delta n(\vec{r},t)$, by the equations

$$\delta n(\vec{r},\omega)=\int d^3r'\,\chi_0(\vec{r},\vec{r}\,';\omega)\varphi^{\mathrm{SCF}}(\vec{r}\,',\omega),$$

$$\varphi^{\mathrm{SCF}}(\vec{r},\omega)=\varphi^{\mathrm{ext}}(\vec{r},\omega)+\int d^3r'\,K(\vec{r},\vec{r}\,')\delta n(\vec{r}\,',\omega).$$

We exactly calculate the retarded density-density response function in the independent-particle approximation, $\chi_0(\vec{r},\vec{r}\,';\omega)$; and the time-independent kernel function is taken to be

$$K(\vec{r},\vec{r}\,')=\frac{e^2}{|\vec{r}-\vec{r}\,'|}+\delta(\vec{r}-\vec{r}\,')\frac{d}{dn}V_{xc}\{n\}|_{n=n(\vec{r})}.$$

$V_{xc}\{n(\vec{r})\}$ is the exchange-correlation potential commonly employed in a local density approximation (LDA) to density-functional formalism.[12] We wish to emphasize that the structure of our calculation is identical to the random-phase approximation with exchange (RPAE)[5,6]; however, we replace the Hartree-Fock orbitals, eigenvalues, and Coulomb matrix elements by LDA orbitals, eigenvalues, and linearized potentials, respectively. The crucial replacement of the nonlocal Hartree-Fock exchange operator by the local exchange-correlation potential is responsible for the spatially local character of $\varphi^{\mathrm{SCF}}(\vec{r},\omega)=\varphi^{\mathrm{ext}}(\vec{r},\omega)+\varphi^{\mathrm{ind}}(\vec{r},\omega)$. In the long-wavelength limit, photoemission cross sections are computed by simply replacing the usual dipole opera-

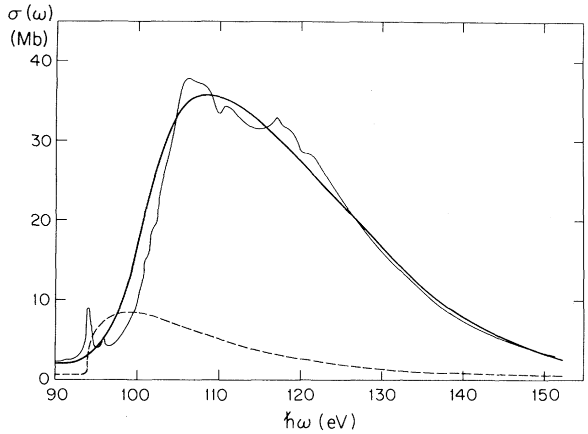

FIG. 1. Total photoabsorption cross section for barium above the 4*d* threshold: Independent-particle calculation (dashed curve); TDLDA calculation (heavy solid curve); data from Ref. 10 (light solid curve), normalized (see text).

tor by $\varphi^{\mathrm{SCF}}(\vec{r}, \omega)$ in a typical Fermi's "golden rule" expression.[9]

Our calculation of the total photoabsorption of barium above the 4*d* threshold along with the vapor data of Rabe, Radler, and Wolff[10] appears in Fig. 1. It is important to note that our calculations contain no adjustable parameters and that the data have been independently normalized to satisfy the *f*-sum rule with ten electrons between 95 and 160 eV.[13] The importance of the induced field is evident by comparison with the independent-particle calculation (dashed line). In Fig. 2 we present our calculations of two valence-level partial photoemission cross sections of barium along with scaled solid-state data of Hecht and Lindau.[14] Recently, generalizations of the RPAE have been able to achieve comparable results,[5,6] but only after relaxation of the electrons around the 4*d* core hole is approximately taken into account. Our calculations do *not* include relaxation effects, and the excellent agreement with experiment we find suggests that such effects need not be explicitly included if one uses a self-consistent field theory based upon the LDA rather than the Hartree-Fock approximation. We do not mean to imply that relaxation is small and unimportant since, for example, ionization thresholds are strongly influenced by the core hole potential and our formalism is intrinsically in error in its prediction of these quantities. The precise role of relaxation in TDLDA calculations remains to be determined.

In our work on the open-shell cerium atom, we have made an approximation typical of ground-state LDA calculations: The open shells are treated as closed with fractional occupancy of the magnetic sublevels. The main effect of this procedure is to produce cross-section curves which smoothly interpolate through any complex threshold behavior due to the several final-state multiplets of the residual ion. Our calculations of several partial photoionization cross sections for cerium are presented in Fig. 3. Three aspects of these curves are particularly striking. First, the emission from the *d* shell is quite

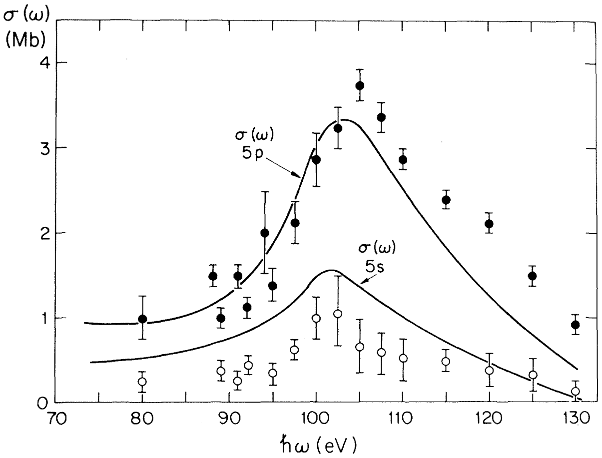

FIG. 2. 5*s* and 5*p* partial photoionization cross sections for barium. The absolute, but not relative, values of the data points (Ref. 14) have been adjusted for best fit to the calculation.

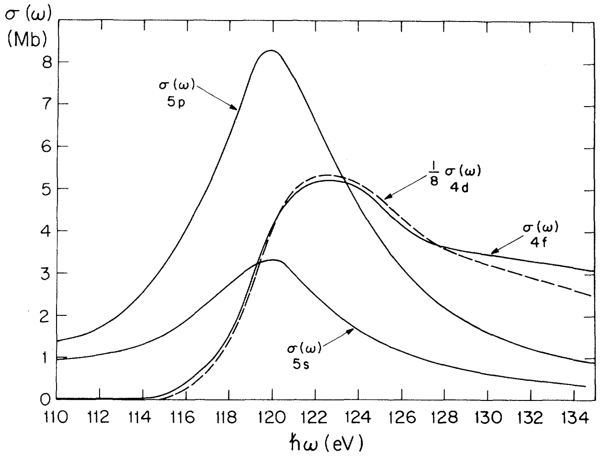

FIG. 3. TDLDA calculations of selected partial photoionization cross sections for cerium near the 4*d* threshold. Note that $\sigma_{4d}(\omega)$ has been reduced by a factor of 8 and nearly overlaps $\sigma_{4f}(\omega)$.

dominant, as it was in the barium case. Second, near the 4*d* threshold, the 4*f* emission almost exactly tracks the 4*d* emission. Third, all the other valence-level partial cross sections (including the 5*d* and 6*s*, not shown) peak at a photon energy which is *lower* than the peak position of the main 4*d* channel. We emphasize that these calculated outer-shell cross sections all peak at the same photon energy.

Indeed, in an experimental study of cerium pentaphosphate,[2] the 5*s* and 5*p* partial cross sections were found to peak at a lower energy than the main absorption and to exhibit line shapes in agreement with our calculations. However, the reported relative magnitude of these cross sections are not in agreement with out results. Regarding the 4*f* emission, Johansson *et al.*[1] and Lenth *et al.*[2] both report a cross section which mirrors the photon energy dependence of the main 4*d* absorption, as we find, although the 4*f*-peak position itself occurs at a slightly lower energy than the 4*d* peak.

A physical explanation of all the phenomena observed in Figs. 1–3 is readily available in terms of the local field $\varphi^{\mathrm{SCF}}(\vec{r},\omega)$. Basically, the oscillations of the ten-electron 4*d* shell control the entire situation. We view the response of the 4*d*-electron density to the external field as much like that of a damped, driven, simple harmonic oscillator. The long-wavelength external field establishes a dipolar disturbance in the electron density, inducing a dipolar field. At some self-consistently determined resonance position, about 123 eV in cerium, this induced field oscillates 90° out of phase with the driving field. The $\langle \epsilon f|\varphi^{\mathrm{SCF}}|4d\rangle$ matrix elements are completely dominated by the induced field and produce a peak in the 4*d* absorption. *Below* resonance, the shell oscillates *in* phase with the external field and the induced dipolar field enhances (or antiscreens) the external field at radial distances exceeding the 4*d*-shell charge radius.[15] At some particular frequency below resonance, the induced field reaches its maximum amplitude (in cerium at about 120 eV). The outer shells, i.e., those with a principal quantum number greater than 4, respond to the sum of this induced field and the external field. The cross sections peak accordingly. Above the 4*d*-resonance energy position, the induced dipolar field reverses direction and these outer shells suffer a screening of the external field with a consequent reduction in their relative cross sections. It should be clear that these considerations apply equally well to the barium case.

The behavior of the 4*f* emission is now simply understood because its radial wave function is practically identical to the 4*d* wave function. A 4*f* electron responds to the local field precisely as a 4*d* electron would near the resonance energy. It is interesting to note that the cerium 4*f* level plays a dual role here. Its very existence is crucial to the enormous polarization of the 4*d* shell, while those spectator electrons actually in residence stream out of the atom in accordance with the local field produced by the virtual transitions to the partially empty shell.

In conclusion, we wish to point out that our view is not inconsistent with the usual interpretation of resonant enhancement effects in the rare earths, i.e., autoionization of the intermediate state $4d^9 4f^{N+1}$ configuration into several decay channels which fill the 4*d* core hole and eject valence electrons.[1-4] Indeed, the relevant matrix elements in such a description are implicitly included in our calculation (within the local exchange-correlation and open-shell averaging approximations). However, we choose to view these virtual transitions as important contributions to the polarizability of the 4*d* shell and prefer to use the spatial and frequency dependence of the local field to provide our physical interpretation.

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Memory Effect in Field Emission from the W-EuS System

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(112) planes of W–amorphous-EuS field emitters exhibit a memory effect in the current-voltage characteristics, the actually drawn current being "locked in." In contrast to Ovshinsky-type memory switches, self-stabilization of the electron current occurs due to negative space charge. Measurements of the electron-spin polarization exclude a thermally induced mechanism. To our knowledge these memory structures are the smallest in solid-state physics.

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Amorphous (glassy) semiconductors are beginning to be understood to such a level that devices with desired properties can now be fabricated. The initial scepticism of both scientists and engineers towards the discovery by Ovshinsky[1] and others[2] has been slowly replaced by an optimistic approach especially because of the considerable recent progress in the physics of glassy materials. We mention here the Ovonics, which are memory devices made of an amorphous thin film of, for example, $Te_{40}As_{35}Ge_6Si_{18}$ sandwiched between two metal electrodes. By applying a voltage greater than the threshold value, these devices switch into a low-impedance state with only a small voltage drop across the structure.

We report in this paper the observation of a memory effect in a system consisting of a tungsten field emitter with an evaporated, highly disordered EuS layer on top of it. The investigation was performed in order to understand the different switching processes that occur within the W/EuS field-emission system,[3] which is also a powerful source for polarized electrons.

We attribute the memory effect to an electronic process. Switching effects involving rare-earth compounds have also been reported for highly doped EuO (Ref. 4) and EuS (Ref. 5). The basic differences of the present structure when compared with those reported so far are the following: (1) The dimensions are very small (1000 times smaller than the Ovonics). It is not even the small field emitter but only its (112) planes which display the effect. (2) Only one electrode is in contact with the insulating amorphous material. (3) The substrate is a single crystal and is atomically clean before the evaporation of the EuS film. (4) The electrons tunnel into the vacuum, and can therefore be analyzed with respect to their spin or energy, thus offering novel possibilities for the investigation of tunneling phenomena.

The experimental setup consists of an apparatus which is basically a modified field-emission microscope with a probe hole in the fluorescent screen for measuring either the electron-spin polarization or the electron current of a selected part of the field-emission pattern. The electron current is detected by an electron multiplier to increase the sensitivity. For spin-polarization analysis the apparatus was connected to a "Mott" detector. The tungsten tip is mounted on a liquid-helium–cooled cold finger with an improved cooling system as compared to the original design,[6] allowing selection of a stable tip temperature in the range 4–50 K. The temperatures above 4 K are obtained by resistive heating with a carbon resistor which is glued to the heat exchanger rather than by reducing the helium flow rate.