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Multiplet Structure below "Threshold" in Appearance-Potential Spectra—Lanthanum $N_{4,5}$

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We present the $N_{4,5}$ appearance-potential spectrum of La. Structure exists at energies lower than the threshold energy for transitions terminating at the Fermi level. Several similarities between optical absorption spectra and our results are discussed. These results contradict the simple model usually used to interpret appearance-potential spectra and emphasize the need for a new theory.

Appearance-potential spectra (APS) of metals can be related to $N(E)$, the density of empty states above the Fermi energy E_F, according to a well-known approximate theory.[1] We hoped, with this technique, to locate the position of the $4f$ states in La, a problem of considerable interest in superconductivity.[2] Since the $4f$ wave functions in La are well localized, we expect a large peak in $N(E)$ around the energy of the $4f$ levels. Such a peak should give a characteristic structure in the APS,[1] which did not appear in the measurements. Instead, we found structure at energies lower than the threshold energy for transitions terminating above E_F. We also observed several similarities between soft-x-ray absorption spectra (SXA) and APS.

We measured the APS of La and Ce in the energy region 0–1300 eV, exciting electrons from the M and N shells. The measurements were made by standard techniques and will be described in more detail elsewhere.[3] The spectrometer is of the type described by Musket and Taatjes,[4] with a Ta photocathode and a V-shaped tungsten filament. The samples were evaporated *in situ* onto a stainless steel substrate at pressures below 1×10^{-8} Torr and data were recorded within a few

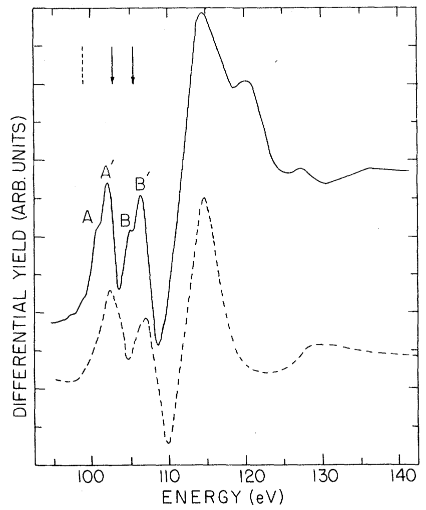

FIG. 1. La$N_{4,5}$ APS. Solid line, clean surface; broken line, contaminated surface. The two arrows pointing down mark the energy for exciting $4d_{3/2}$ and $4d_{5/2}$ electrons to E_F (from Ref. 6). The dashed arrow is the same but from Ref. 7. (A 4.5-eV correction for the work function, but no other correction, has been applied to these data.)

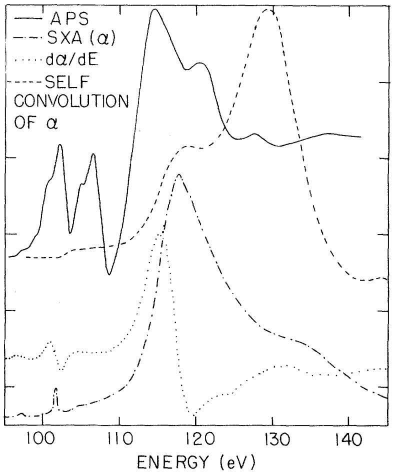

FIG. 2. Calculated APS spectra according to several models. Solid line, measured APS; broken line, theory of Ref. 1 and our Eq. (1); dot-dashed line, $\alpha(E)$ from Ref. 11; dotted line, $d\alpha/dE$.

minutes after evaporation at pressures near 5×10^{-10} Torr. The spectra remained reproducible for several hours.

Data from our first films of both La and Ce were similar to those of Harte, Szczepanek, and Leyendecker[5] in the $M_{4,5}$ region, but after several evaporations were performed from the same source, we observed a change in both the energies and line shapes of the $N_{4,5}$ as well as of the $M_{4,5}$ regions. Simultaneously, the spectra of contaminants, principally oxygen and carbon, went below the sensitivity of our apparatus. We believe that the source material, originally contaminated, preferentially lost impurities during successive evaporations. This hypothesis was partially tested by using a recently produced piece of La, one presumably less oxidized, whose purity was analyzed prior to use. In this case, we obtained the final spectra after only a few evaporations.

The $N_{4,5}$ APS of La, shown in Fig. 1 for both clean and contaminated films, cannot be explained in terms of the theory resulting in Eq. (1). The APS measures the energy derivative of the bremsstrahlung and the total yield of x-rays emitted by the radiative decay of a core hole created by the inelastic scattering of an electron incident with energy E. The total yield is proportional to the probability for a transition from the ground state to an excited state of the system formed by the crystal and the incident electron. Assuming constant matrix elements, one-electron energy bands, and unbroadened core levels, one obtains for metals the simple result that the measured signal $A(E)$ is related to $N(E)$ by[1]

$$A(E) \sim \frac{d}{dE}\int_0^{E-E_t} N(\epsilon)N(E-E_t-\epsilon)\,d\epsilon, \tag{1}$$

where ϵ is the energy of a final electron measured from E_F, and E_t is the energy to excite a core electron to the Fermi level. Under the same assumptions, the optical absorption coefficient $\alpha(E)$ is proportional to the density of final states, $N(E-E_t)$. Substitution in Eq. (1) gives

$$A'(E) \sim \frac{d}{dE}\int_0^{E-E_t} \alpha(\epsilon+E_t)\alpha(E-\epsilon)\,d\epsilon, \tag{2}$$

which can be evaluated numerically to predict an APS line shape. There are two major discrepancies between our data and this simple theory. First, much of the structures labeled A, A' and B, B' (Fig. 1) occurs at energies lower than E_t, which is precluded by Eq. (1). Second, using available data[8-11] with Eq. (2), we obtain a result (the dashed curve in Fig. 2) completely different from the measured spectrum.[12]

It has been shown[13-16] that in the case of rare earths, the oscillator strength for the optical excitation of $4d$ electrons is concentrated in the $4d^{10}4f^N \to 4d^94f^{N+1}$ transitions. The final-state configuration is split into a multiplet spread over

20 eV as a result of the large exchange interaction between the $4d$ hole and the $4f$ electron. Some of these levels lie above the ionization threshold. Transitions to them contain most of the oscillator strength and are broadened into a continuum by autoionization. The other levels give rise to the sharp peaks below threshold. The calculations were performed for the tripositive ions, but they explain very well the SXA of rare-earth metals[8-11] as well as of rare-earth compounds.[17] This interpretation of the observed spectra, given in terms of the oscillator strength of atomic-like transitions rather than in terms of interband transitions, invalidates the approximations leading to the relation $\alpha(E) \sim N(E-E_t)$, and the simple picture of Eq. (1) also must be discarded.

In the excitation process, the initial state can be formed from the crystal ground state and the state of the incident electron. Let us assume first, based on the very localized nature of the La $4f$ wave functions, that the final state is formed by an excited state of a particular ion plus the state of the extra electron far from that ion and not interacting with it. Therefore, both SXA and APS are probing, with different tools, the same excited states of a rare-earth ion, and the two types of spectra should have common features. Actually, we find several similarities between the La $N_{4,5}$ SXA[8-11] and our spectra. They both show narrow structures below E_T, corresponding to the excitation of the bound states $^3P_1$ and $^3D_1$ of the $4d^94f$ configuration.[13-16] The energy difference between the sharp lines is the same for APS and SXA, although the lines occur at higher energies in the APS. The broad band present above threshold in both APS and SXA can be attributed to the excitation of the strong $4d^94f$ $^1P_1$ resonance.

The differences between SXA and APS must reflect the presence of the extra electron in APS. In the approximation of a noninteracting final state mentioned above, when a bound state of the $4d^94f$ configuration of a La ion is excited with fixed energy, E_b, the scattered electron scans through the density of final states as E is increased. When its energy, $E-E_b$, is sufficient to penetrate the centrifugal barrier of the empty $4f$ states of a different ion, there should be a resonance in the scattering cross section and corresponding structure in the APS. In the $N_{4,5}$ APS of La we observe a step at ~97.2 eV, which we interpret as the excitation threshold E_b for the $^3P_1$ state, in agreement with SXA. This is followed by the pair of structures A and A' at 3.8 and 5.2 eV above the optical peak, one or both of which should correspond to the previously mentioned $4f$ resonance. The same separations occur between peaks B and B' and the absorption peak at 101.7 eV,[8-11] with the exception that we do not resolve the step at the threshold E_b. Liefeld, Burr, and Chamberlain[18] observed a single peak 5.5 eV above E_F in the bremsstrahlung and bremsstrahlung isochromat spectra of La. Our contaminated films gave spectra with single peaks at approximately this energy above their optical partners. In this case, however, the threshold at E_b has shifted to higher energy. Such a shift was also observed in the $N_{4,5}$ APS of Ba.[19]

The splitting of these structures observed in the APS of clean samples is not yet well understood. It does not appear to be caused by a mixture of pure metal and oxide. We find that either the relative strengths of the two components is always the same, or there is no splitting at all and the peak is at higher energy. The splitting could arise from the excitation with and without the scattered electron's remaining nearby. Wendin[20] calculated for Ba atoms a lower average resonance energy for the scattered electron to penetrate the $4f$ centrifugal barrier if the electron is near and interacting with the excited atom. Since both situations can occur, this results in double structures in the APS. If this is the case, structures A and B in Fig. 1 can be associated with the "interacting" case, while structures A' and B' correspond to the "noninteracting" case. However, the final configuration of the excited ion containing an extra $4f$ electron is $4d^94f^2$ and should show a multiplet structure similar to that of an excited Ce ion. Such multiplet structure is not found.

Above threshold the shape of the derivative of $\alpha(E)$, $d\alpha(E)/dE$, resembles the APS (as shown in Fig. 2). It is well known that the inelastic scattering of electrons of several keV of energy traversing a medium is well described by the loss function $|\text{Im}1/\epsilon(0,E)|$.[21] $\epsilon(0,E)$ is the dielectric function of the medium with zero momentum transfer. Assuming that the same picture holds even for electrons of about 100 eV,[22] we find that the excitation probability, whose derivative is measured by APS, is proportional to $\alpha(E)$ through the relation $|\text{Im}1/\epsilon| \approx \epsilon_2 \propto \alpha/E$, which is valid at 100 eV since $\epsilon_2 \ll \epsilon_1 \approx 1$.

We have shown that the La $N_{4,5}$ APS does not follow at all the simple theory of Ref. 1. We have tried to explain some of the observed features by comparing APS and SXA, and we are aware that some of the assumptions we have used are too crude. It is clear from the foregoing that the next step should be a calculation similar to those in Refs. 13–16 for a rare-earth ion with the addition of a nearby electron, or a calculation similar to that of Wendin,[20] but with the inclusion of multiplet structure.

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Parametric Coupling in an Optically Excited Plasma in Ge

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Recent measurements of apparent absorption saturation and ultrafast relaxation in Ge have been reinterpreted as a parametric coupling between optical beams due to an index grating produced by a high-density electron-hole plasma. A sharp spike in probe-beam transmission of width 2 psec observed near zero time delay between a strong pumping and a weak probing beam has been shown to be the autocorrelation of the optical electric fields. In addition, evidence of a true saturation effect with a much longer recovery time is observed.

Recently the optical properties of germanium have been the subject of investigation on a picosecond time scale.[1,2] Kennedy *et al.*[1] have reported measurements of the nonlinear absorption of Ge from which they infer an ultrafast carrier relaxation time. They have observed an apparent saturation of the absorption of 1.06-μm picosecond pulses in thin Ge crystals at high optical intensities. The recovery time of the absorption was observed to be less than the optical pulse