f-f Excitations by Resonant Electron-Exchange Collisions in Rare-Earth Metals

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The spin-forbidden f-f multiplet excitations are observed for the first time as the strongest features in the electron-energy-loss spectra of Gd, Dy, and Sm metals at low primary-electron energies. The exchange nature of the excitation process is argued, in analogy with that of spin-flip Stoner excitations in d-band ferromagnets. A resonance enhancement observed for primary-electron energies near the $4d$-$4f$ core threshold is found to be consistent with the proposed mechanism.

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Spin-forbidden excitations by electron-exchange collisions, long known in atomic physics,[1] have recently been rediscovered in solid-state physics. Yin and Tosatti[2] and Glazer and Tosatti[3] have given the first simplified theoretical description of this process in a band ferromagnet. Hopster, Raue, and Clauberg[4] and also Kirschner, Rebenstorff, and Ibach[5] have shown by (spin polarized) electron-energy-loss spectroscopy (EELS) that spin-flip Stoner excitations across the exchange gap of Fe and Ni can be observed via this mechanism. More recently, we have demonstrated[6] that such transitions can also be identified by ordinary, not spin-polarized, EELS, as predicted in Ref. 3. It is clearly of interest to extend such a study to the rare-earth metals.

In rare-earth metals the situation is in principle rather different, with correlated f levels replacing the d bands. The Stoner excitations, in particular, are here replaced by f-f multiplet transitions. Such transitions are expected to be now largely independent of temperature, and generally also of lattice effects, because of their strong intra-atomic nature. Like the Stoner excitations, however, the f-f transitions are optically invisible in pure metals, being spin forbidden. A typical example is Gd, where the lowest excited-state multiplets are ^6P, ^6D, ^6F, ^6G, ^6H, and ^6I, while the ground state is ^8S. These f-f transitions become very weakly allowed and barely observable (oscillator strength 10^{-6}) in ionic configurations without inversion symmetry.[7]

The purpose of this Letter is to show for the first time that such rare-earth-metal f-f transitions not only become allowed by electron-impact excitation, but in fact constitute the dominant feature of low-energy EELS (momentum integrated) spectra. Evidence is provided that the f-f excitation occurs via an electron-exchange process, very much like the d-d Stoner excitations in Fe and Ni. Furthermore, we demonstrate how in Gd this excitation process is resonantly enhanced when the primary-electron energy reaches the $4d$-$4f$ core threshold near 140 eV. This process constitutes the direct analog of the resonant photoemission.[8] In the present EELS case, however, a new situation arises, where *two* f electrons are simultaneously added to the same atom, instead of one, as in resonant photoemission.

Experiments were performed at a pressure of 2×10^{-10} mbar. The samples were cleaned by Ar^+ sputtering each time that the surface contaminant coverage increased above 5% of a monolayer. No difference has been observed between spectra taken in this condition and others taken with simultaneous sputtering. The electron beam impinged onto the sample surface with an incidence angle of 30°. The backscattered electrons were collected in a 12° cone along the normal to the surface and analyzed by a hemispherical mirror analyzer with a total energy resolution of 0.5 eV. Because of this large cone and because of the large surface roughness, all scattering angles are integrated in our experiment. The primary-electron energies were referred to the electron-energy-analyzer vacuum level, and were measured with an accuracy of ±0.5 eV.[9]

Figure 1 shows several well-defined, perfectly reproducible low-energy structures, the strongest at 4.5, 6.9, and 10–12 eV with weaker substructures at 5.2, 6.3, and 7.3 eV. All of this structure, except for the broad 12-eV peak, is absent in the $\mathrm{Im}(1/\epsilon)$ function of Gd, obtained either optically[11] or by transmission of fast electrons,[12] and in the spectra taken with primary energy $E_P \geq 500$ eV. Straightforward comparison with well-known spectra of Gd^{3+} ion[7] allows their identification as f-f excitations. This is further confirmed by the very close similarity of our Gd data to the x-ray photoemission spectrum of Tb metal of Lang, Baer,

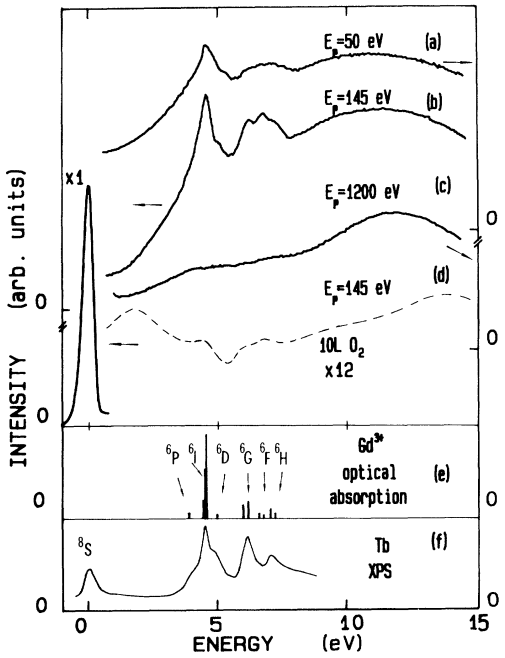

FIG. 1. Energy-loss spectra of clean Gd at values of E_P of (a) 50 eV, (b) 145 eV, and (c) 1200 eV, and of (d) oxidized Gd {10 L of O_2 [1 langmuir (L) $= 10^{-6}$ Torr sec]} at $E_P = 145$ eV. (e) Optical absorption of Gd^{3+} ion showing the components of the f-f transition multiplet (from Ref. 7). (f) X-ray photoemission spectrum of Tb (from Ref. 10) showing the same multiplet. The energies are referred to that of the ^8S peak and the spectrum is contracted by 10% following Ref. 10. The abscissa scale refers to energy loss ω for the curves (a)–(d), to photon energy for (e), and to binding energy for the curve in (f).

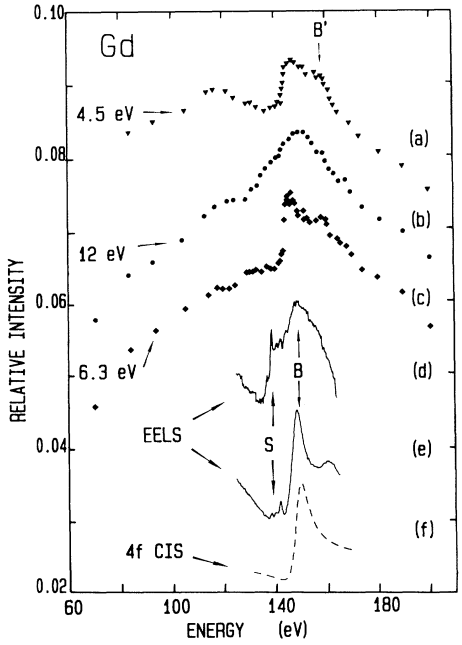

FIG. 2. Intensity of the (curve a) 4.5-eV loss, (curve b) 12-eV "plasmon" loss, and (curve c) 6.3-eV loss normalized to that of the elastic peak. Curve d, $4d$-$4f$ core threshold in energy loss with $E_P = 210$ eV. Curve e, same as curve d but with $E_P = 2000$ eV. Curve f, $4f$-photoemission intensity [constant initial state (CIS)] as a function of photon energy (from Ref. 8). The abscissa scale refers to primary energy E_P for curves a–c, to energy loss ω for curves d and e, and to photon energy for curve f. For the sake of clarity curve a has been shifted upwards by 0.007 unit.

and Cox[10]: Since the f electrons are akin to core electrons, the photoemission spectrum of the $Z+1$ element and the inverse photoemission spectrum of the $Z-1$ must both be closely similar to the neutral excitation spectrum of the Z element.[10] Particular care was taken in checking that our new features are indeed characteristic of clean Gd, rather than, e.g., an oxidized Gd surface. Deliberate oxidation leads in fact to rather different features, also shown in Fig. 1.[13] Hence, we conclude that we have observed the spin-forbidden f-f excitations of Gd metal, a process that can only take place via electron exchange.

In order to clarify this point, we have proceeded to study the primary-electron energy dependence of the excitation process. Part of the motivation for doing this comes from the analogy to the band-ferromagnet case. There, this dependence is sufficiently strong and characteristic to allow a direct pinpointing of exchange spin-flip transitions, even without spin-polarization analysis.[6] The relative EELS rates at 4.5, 6.3 (f-f transitions), and 12 eV (plasmon peak[10,11]), normalized to the elastic peak intensity, are shown in Fig. 2. The f-f transitions display a remarkable *resonant* phenomenon. They are sharply enhanced by the onset of the $4d$-$4f$ core threshold, giving rise to a two-peak behavior, with a sudden jump at 144 eV and peaks at 147 and 157 eV (broad feature B').[14] We simultaneously locate the core $4d$-$4f$ transitions by EELS and find the well-known sharp resonances S at 138 eV, and the large broad peak B around 148 eV.[15] As Fig. 2 shows, the narrow resonances S are about as important at low E_P as the broad absorption peak B. At higher E_P, however, only the peak B survives.[16] It actually also picks up what very probably is an extrinsic plasmon satellite, at about 161 eV. The $4f$ photoemission intensity of Gd, also shown in Fig. 2 as a function of photon energy, is similarly dominated by the broad peak at 149 eV[8] (no plasmon satellite in this case). The broad band B corresponds to strongly dipole-allowed $4d^{10}4f^7 \rightarrow 4d^9 4f^8$ transitions, while the sharp features S, at excitation energies less than 145 eV, are weakly dipole-allowed transitions of the same kind.[17] They are enhanced in the low-E_P ($E_P \leq 300$ eV) EELS spectra probably also by an exchange process,[16] as we

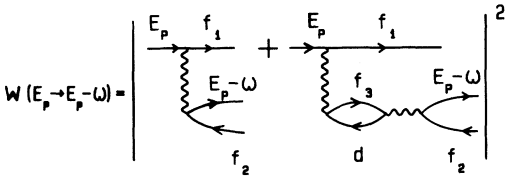

FIG. 3. Schematic representation of the matrix element of the exchange process which gives rise to the observed multiplet. The second term is responsible for the resonance behavior.

plan to discuss elsewhere.[18]

As Fig. 2 shows, the f-f transitions become resonantly enhanced when E_P reaches the threshold for the strongly allowed $4d$-$4f$ core transitions (B). We interpret this as due to the constructive addition to the ordinary exchange EELS amplitude of a resonant counterpart, as shown schematically by the diagrams of Fig. 3. The resonant process occurs by first dropping the incident electron into an empty f state (f_1) (whereby $f^7 \rightarrow f^8$) and then by promoting a core $4d$ electron to the same f shell (f_3) ($f^8 \rightarrow f^9$). In the corresponding resonant x-ray photoemission process there is no primary electron, and the core electron is promoted to f^8 only. The additional intra-f-shell repulsion involved may explain the additional bump B′, located some 10 eV higher than B. This bump is unrelated to either spin-orbit effects (which would be visible in curve f—the $4f$ CIS spectrum) or to the extra bump in EELS (curve e), which is present only for high E_P and therefore is almost certainly an "extrinsic" plasmon excitation.

We stress that while the finding of a core resonance does not in itself prove the exchange nature of the bare (nonresonant) f-f transitions, it does independently and naturally fit into this picture. In other words, if the f-f excitations were of ordinary, dipole-like nature, they could not be resonantly enhanced as such, since the energy exchanged by the virtual photon is in that case ω, rather than $\sim E_P$.

All of the above should clearly not be peculiar to Gd alone. We have performed similar, though less extensive measurements also on Sm and Dy, and indeed find a very similar picture. Leaving details for a later, longer paper,[18] we show in Fig. 4 the EELS spectra of Sm and Dy, which also show clear f-f transitions. These transitions are also similarly enhanced at the corresponding $4f$-$4d$ threshold. When the f shell is not half filled, f-f excitations without spin flip are also possible.[18,19] These transitions are clearly present in the Dy EELS spectrum, where they contribute at $\omega < 1.5$ eV and at $\omega = 3.5$ eV.[19]

We stress again that our experimental conditions imply that our spectra are momentum integrated. Now, it is important to bear in mind that the f-orbital angular momentum is not quenched in the metallic crystal. Thus, the full multiplet of excited states ^6P, ^6D, ^6F, ^6G, ^6H, and ^6I can be reached by large-angle scattering (and observed by angle-integrated EELS), while (in the absence of spin-orbit coupling) none of these states could be reached from the ^8S ground state in a forward-scattering experiment. In actual fact a single weak peak has been observed in spin-polarized, angle-resolved forward-scattering EELS spectra by Weller and Alvarado.[20] The preferential excitation with incoming spin-up electrons should be accountable for by the presence of spin-orbit coupling. Spin-orbit coupling is crucial in this case, in allowing a trade-off between spin and orbital angular momentum that can make the $^8S \rightarrow {}^6P$ transition (~ 4 eV) weakly allowed even in forward scattering. Based on our results and on these considerations we predict that the entire f-f multiplet, as we observe it, would also gradually emerge from an angular-resolved EELS experiment for increasing momentum transfer.

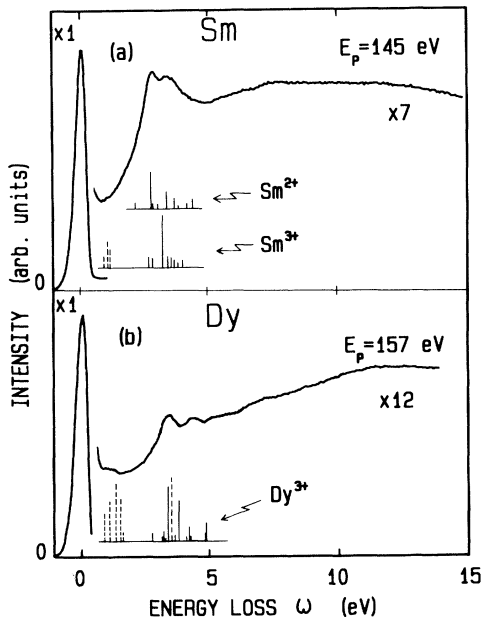

FIG. 4. (a) EELS spectrum of Sm. Also shown are the trivalent- and divalent-ion f-f transitions observed in optical absorption (from Ref. 7). Note that the Sm surface is in a mixed-valence state. (b) EELS spectrum of Dy compared with the trivalent-ion f-f optical transitions (from Ref. 7). Transitions without spin flip are shown by dashed bars.

In summary, we have found for the first time that spin-forbidden f-f excitations of rare-earth metals can be observed by ordinary EELS, via an electron-exchange process. This process, in turn, is resonantly excited at the $4f$-$4d$ core threshold by a mechanism analogous to resonant photoemission, where, however, as many as two extra electrons can be added to the

same f shell.

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