thin-film niobium samples, which cannot be adequately described by the hot-spot theory, has been described in terms of the "healing" of a quasiparticle-induced gap inhomogeneity.

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Divalent Surface State on Metallic Samarium

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It is shown that the first atomic layer of trivalent metallic samarium has a large divalent component. The valence transition is attributed to a narrowing of the 5*d* band which populates the low-lying $4f^6$ state.

The existence of a unique, resolvable signal from the first layer of atoms in core-level spectroscopies has long been anticipated but never successfully demonstrated.[1,2] On the other hand, surface states have been identified in many photoemission experiments.[3] We report here the first example, metallic samarium, in which a spectrum of surface atoms has been resolved and identified in photoemission from both core and valence states. The detection was made possible by a valence transition at the surface.

The fact that a divalent signal appears in the spectra of Sm metal has recently been pointed out,[4] but the question of whether it is a bulk or surface phenomenon was left open. The initial identification was made in the 4*d* spectrum, on the basis of comparisons with the spectra of trivalent SmSb, divalent SmTe, and intermediate-valence SmB_6. The overlap between the 2+ and 3+ spectra, as well as the complex multiplet structures make the 4*d* spectrum less attractive for detailed analysis than the simpler 3*d* spectra. It is well known, however, that the 3*d* spectra of insulating compounds of La, Ce, Pr, and Nd have strong, final-state, charge-transfer satellites due to valence-band–to–$4f$ transitions.[5] The possibility of analogous conduction-band–to–$4f$ transitions in the metals casts some doubt on the utility of the $3d$ spectra for the characterization of the initial-state valence. Recent studies have shown, however, that such satellites remain weak in the metals because of the effective screening by $5d$ conduction electrons.[6]

The experiments were performed with monochromatized Al $K\alpha$ radiation in an HP 5950A spectrometer, modified for UHV operation. Samarium metal was evaporated onto stainless steel or gold-plated substrates with surfaces tilted relative to the 52° orientation required for dispersion compensation. The loss of resolution inherent in this procedure is not significant for the relatively broad lines considered here. Data were taken only during the first hour after evaporation, because some oxygen could be detected after that period. The core levels remained largely unaffected for longer periods.

Tilting the surface normal away from the direction of electron collection enhances emission from the surface relative to that from the bulk. It serves to distinguish between emission from bulk and surface atoms, but not betwen final-state charge-transfer effects and initial-state mixed-valence behavior. The latter discrimination can be made with certainty only on the basis of $4f$ spectra. In either case the two states found in core-level spectra are separated not by the Coulomb correlation energy, but by the binding energy of the $4f^{n+1}$ level in the final-state valence band.

The $3d$ spectra appear to be simple because the multiplet interaction with the $4f$ shell is much smaller than the 27.5-eV spin-orbit splitting, and not much greater than the linewidth itself. In Fig. 1(a) we show a wide scan of the $3d$ region taken at the standard sample orientation, with the divalent and trivalent components identified.[7] Figure 1(b) shows the $3d_{5/2}$ region in greater detail for three different takeoff angles (measured from the surface normal). The 42° and 75° data have been scaled so as to give the divalent components between 1070 and 1080 eV the same amplitudes. (The shapes are then also identical.) The amplitude of the trivalent component, measured above background, is seen to increase with decreasing takeoff angle. It is therefore immediately clear that the two components come from different spatial regions of the sample, ruling out the possibility that bulk Sm metal is itself in an intermediate-valence state.

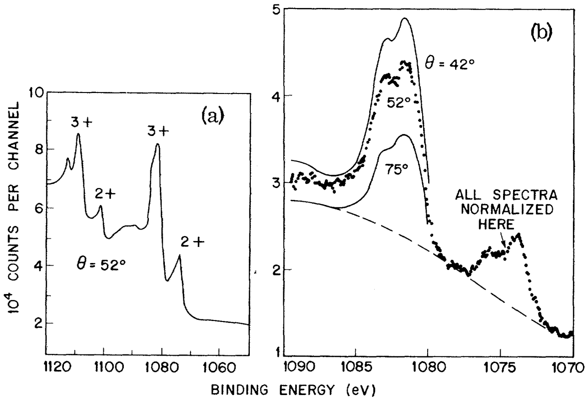

FIG. 1. X-ray photoemission spectra of the $3d$ region of vacuum-evaporated samarium: (a) wide scan showing the complete spin-orbit structures; (b) the $3d_{5/2}$ region at three different sample orientations.

The doublet structure of the peaks does not change with takeoff angle indicating that it is an intrinsic, bulk property, undoubtedly representing the effect of $3d$-$4f$ multiplet coupling. The separation between the 2+ and 3+ peaks is 7.6 eV, i.e., larger than the Coulomb correlation energy in Sm metal which is ~5.8 eV.[8,9] Using an equivalent-cores argument, in which trivalent, core-ionized $3d^9$ samarium is represented by quadrivalent europium, this separation should be given by the binding energy of the f^6 state of Eu^3 in Sm metal. Unfortunately there are no calculations for the latter, but an interpolation in the calculation of Herbst and co-workers[8,9] based on the results for trivalent Sm and Gd yields a value of ~7 eV for the binding energy of Eu^{3+} in a trivalent lattice. This estimate is in satisfactory agreement with the measured (2+)-(3+) separation in the $3d$ spectrum.

To facilitate further analysis we initially make the simple assumption that the Sm^{2+} is entirely located within a uniform divalent surface layer of thickness, a. The ratio of trivalent to divalent signal is then

$$R(\theta) = [\exp(a/\lambda\cos\theta) - 1]^{-1}, \tag{1}$$

where λ is the mean free path of the photoelectron for inelastic scattering. This "escape depth" is estimated to be 6 Å at the 400-eV kinetic energy obtained by photoexciting the $3d$ shell with Al $K\alpha$ radiation. The ratios obtained from the data shown, $R(42°) = 3.6$, $R(52°) = 3.0$, and $R(75°) = 1.8$, are not compatible with Eq. (1) because the change with angle is too slow. (A reduction of the effective angle from 75° to 62° would be required to account for the observations.) This could in principle be due to surface roughness which tends to decrease the effective takeoff angle, especially at large angles. Alternatively, the slow variation of $R(\theta)$ could simply arise from the fact that the surface layer is not entirely divalent but is an intermediate-valence state. Based on the behavior of SmB_6 or collapsed SmS, this is not an unreasonable hypothesis. With this generalization Eq. (1) takes the form

$$R(\theta) = \{1 - \alpha + [\exp(a/\lambda \cos\theta) - 1]^{-1}\}/\alpha, \qquad (2)$$

where α is the fractional divalent component of the atoms in the surface layer. Satisfactory agreement with the experimental ratios is obtained for $\alpha = 0.4$ and $a = \lambda/2$, i.e., the average valence is 2.6 and the surface layer is 3 Å or one atomic layer thick. The estimate of α could be substantially affected by surface roughness, but the general conclusions that the divalent samarium is confined to the outermost atoms is considered to be reliable.

In order to determine whether the divalent samarium is an initial-state surface feature or a final-state satellite, we consider the $4d$ and valence-band spectra. In fact, it was the sharp peak at 123 eV in the $4d$ spectrum [see Fig. 2(b)] which first suggested the possibility of intermediate-valence behavior in the surface or bulk of metallic Sm. (Charge-transfer satellites are expected to be much weaker in the $4d$ spectra.) The analysis of the $4d$ data is, however, more difficult because of the complex multiplet structure of Sm^{3+} and the strong plasmon energy-loss tail. Moreover, part of the 2+ spectrum is hidden under the stronger 3+ structure. Area ratios are therefore difficult to extract, but qualitatively the increase in 3+ emission at smaller takeoff angle is comparable to that in the $3d$ spectra. Because of the larger escape depth for 1360-eV (kinetic energy) electrons, the angular dependence is actually expected to be weaker than for the $3d$ electrons.

In a sense, the most critical test is provided by the $4f$ spectrum in the valence band. Here, there is no possibility that a divalent component could arise in the final state from $5d \rightarrow 4f$ transitions. On the other hand, a divalent $4f$ spectrum would appear close to the Fermi energy, superimposed on the conduction band of the trivalent metal, making a clean separation of the two somewhat problematical. Nevertheless, valence-band spectra taken at the three angles and normalized at the peak 1 eV below the Fermi energy again show an increased 3+ intensity with decreasing takeoff angle. The effect is, however, considerably reduced because no correction was made for the Sm^{3+} conduction band under the 2+ spectrum (see Fig. 3). The divalent samarium is therefore clearly present in the initial-state and not a final-state satellite.

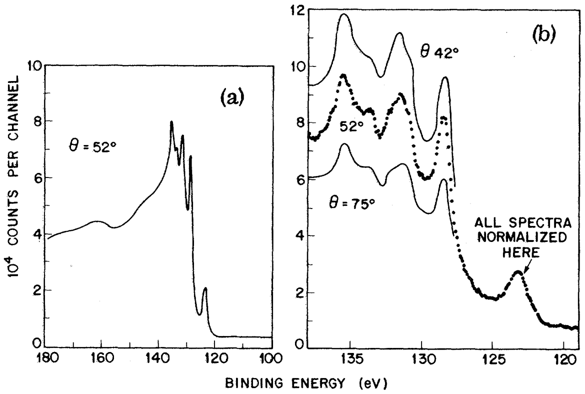

FIG. 2. Spectra of the $4d$ region: (a) wide scan; (b) the effect of surface tilt.

The origins of the unusual valence instability of metallic Sm can be found in the calculations of Herbst and co-workers[8,9] which show that the energy required to promote a d conduction electron from the Fermi energy into an empty $4f$ state is only ~0.2 eV in metallic Sm. Any perturbation which raises the Fermi level by this amount will cause electrons to flow into the $4f$ level. This could in principle be accomplished in the bulk by

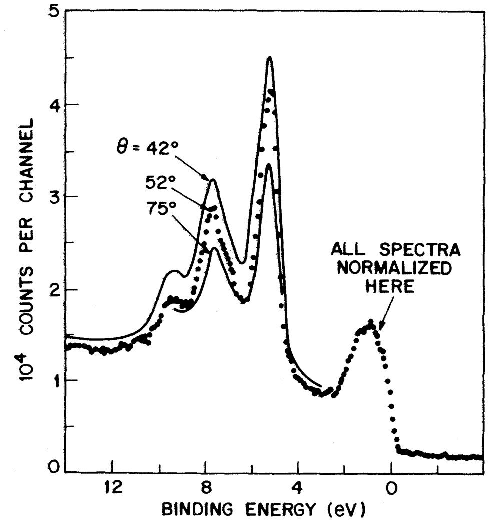

FIG. 3. Spectra of the conduction-band and $4f$ region. The effect of tilting the surface is indicated.

alloying with an element which either donates extra electrons into the d band or causes a lattice expansion narrowing the d band. At the surface, we expect the $5d$-band structure to be perturbed by virtue of the change in local symmetry and the reduction of the coordination number, z. It is not clear without detailed calculations which of these mechanisms is dominant. It is easy to see, however, that a narrowing of the d band by virtue of the reduced coordination number (bandwidth is assumed proportional to $\sqrt{z}$) would raise the Fermi energy and begin to populate the $4f^6$ state. This in turn would cause an expansion of the lattice, resulting in further band narrowing. In this way a relatively small perturbation could result in an instability leading to the intermediate-valence state which is experimentally observed. More detailed theoretical treatment is clearly needed to provide an understanding of this surface-valence transition.

It is natural to inquire whether this phenomenon is likely to occur in other elements. Among the rare-earth metals only thulium has a similar low-lying empty $4f$ state,[8,9] but the excitation energy is ~1 eV, making it less likely to have a spontaneous surface-valence transition. Other examples may be found among the intermetallic compounds of trivalent samarium and ytterbium.

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Frequency Dependence of the Spin-Spin Relaxation Rate from Mössbauer Spectroscopy

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The frequency dependence of the relaxation parameter which determines the line shape of the Mössbauer spectrum in spin-spin relaxation is derived directly from the experimental spectrum for the case of the 84-keV resonance of ^{170}Yb in $Cs_2NaYbCl_6$. The scale of the frequency variation of its relaxation parameter is in agreement with a theoretical estimate.

Theoretical treatment of Mössbauer hyperfine spectra in the presence of electronic relaxation characterizes, by a correlation time τ_c, the fluctuation of the electromagnetic field acting on the Mössbauer atom. These fluctuations then cause relaxation processes in the atoms electronic shell which are described by the relaxation time τ_r. Most present theories[1-4] deal with the limiting case where τ_c is much shorter than either τ_r or the "precession time" τ_L of the nuclear spin in the hyperfine field ($\tau_L = \hbar/A$, with A = hyperfine coupling constant). Both conditions, are safely fulfilled in spin-lattice processes[1] where, for example, $\tau_L \approx \hbar/k_B\Theta$ (Θ = Debye temperature) and