New Metastable Nonmetallic Phase of Europium

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Metastable, close-packed films of elemental, divalent Eu from about a half to several monolayers thick on several substrates were found to be nonmetallic. Photoemission showed no states within 1.4 eV of the Fermi level. Low energy electron diffraction studies of Eu films on Ta(110) showed a close-packed pattern with orientational epitaxy. With increased thickness this phase reverted to metallic bcc Eu with orientational epitaxy.

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Divalent metallic elements may not form metals if they form covalent bonds (e.g., α-Sn) or fill a band that is separated by a gap at all wave vectors from the next higher band (no previously known examples). In the following we report on a metastable phase of divalent Eu which is not metallic and which is close packed in structure, at least in two dimensions. Eu is usually a bcc metal. The ion cores are divalent ($4f^7$), rather than trivalent ($4f^6$), because of the high stability of the half-filled $4f$ shell. Trivalent Eu occurs in some compounds, e.g., $\mathrm{EuF_2}$ and $\mathrm{EuF_3}$ both are known. Photoelectron spectra of the valence and $4f$ electrons of Eu metal have been measured and discussed several times [1,2], and the spectra conform to expectations [3]. We report here very different photoelectron spectra from some Eu films, spectra which show these films are nonmetallic for thicknesses up to several monolayers, not just at submonolayer thickness where interatomic distances may be large. Partial yield spectra of the region of the $4d \rightarrow 4f$ resonance indicate all our samples were divalent Eu, i.e., $4f^7$. Low energy electron diffraction (LEED) studies made on such films grown on Ta(110) showed they were close packed in the plane, not bcc, and there was orientational epitaxy with the substrate. Making these films thicker caused a transition to the metallic bcc phase, with an unusual (110) orientational epitaxy on the incommensurate Ta(110) substrate. Addition of certain impurities drove the nonmetallic films into the bcc phase, indicating the new phase is metastable.

Vacuum-outgassed Ames Laboratory Eu was evaporated as a polycrystalline film onto polycrystalline Ta (both clean and covered with the native oxide), and stainless steel substrates, and as an epitaxial film onto a Ta(110) substrate. Pressures during evaporation did not exceed a few times 10^{-10} Torr, and measurements were made under pressures in the 10^{-11} Torr range.

Photoelectron spectra were taken with an angle-integrating (cylindrical mirror analyzer) electron spectrometer using synchrotron radiation from Aladdin as the source. The overall resolution in the valence band region was about 200 meV. The beam line [4] permitted simultaneous studies of core levels and the valence band. We discuss the 30–300 Å polycrystalline films first. The films grew continuously. The substrate core-level spectra disappeared rapidly and continuously; there was no evidence for cluster or island formation.

Figure 1 shows an energy distribution curve (EDC) and a comparable spectrum from previous work, a spectrum we also could obtain either by evaporating more Eu onto the sample of Fig. 1 or by evaporating a small amount (submonolayer) of impurity (Sm, Cu) onto it. In the latter case, the core lines of the impurity rapidly disappeared, apparently as the impurity diffused into the Eu, and the spectrum changed from the solid curve to the dashed. As can be seen in Fig. 1, in addition to differences in the valence band region, the spectra are different in the $5p$ region and in the inelastic scattering background between the $4f$ and $5p$ regions. The latter two will be described elsewhere [5]. They arise from $4f$ shakeup excitations previously observed in Eu and Gd [6–9]. Figure 2 shows EDCs taken at several photon energies in the valence-band-$4f$ region for a metastable phase of a polycrystalline Eu film on polycrystalline Ta. The most striking feature of the new phase in Figs. 1 (solid line) and 2 is the lack

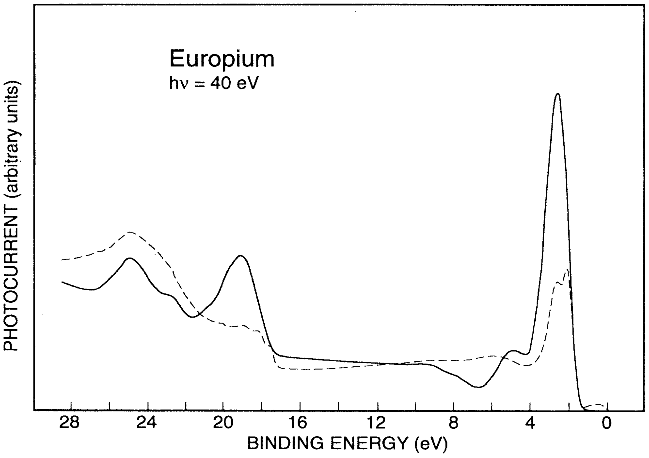

FIG. 1. Photoelectron energy distribution curves taken at 40 eV photon energy for a 50–100 Å thick polycrystalline Eu film, shown solid, and from bcc Eu, shown dashed.

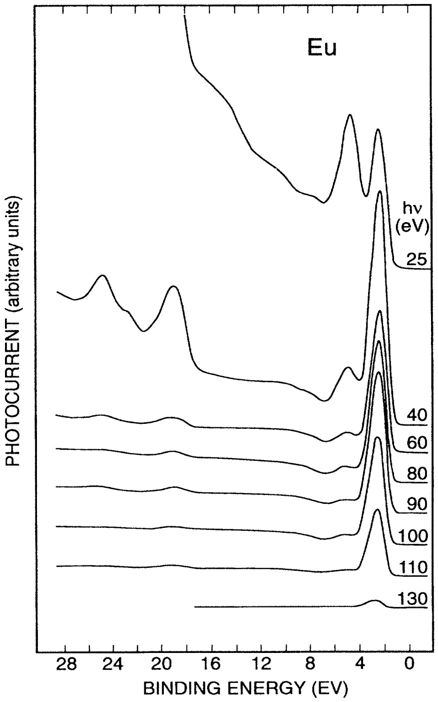

FIG. 2. Photoelectron energy distribution curves for a 5–100 Å thick polycrystalline film of Eu on polycrystalline Ta taken at several photon energies.

of photoelectrons in the first 1.4 eV below the Fermi level, which is known from spectra from the neighboring substrate.

This new phase is not a compound of Eu. X-ray photoemission spectroscopy (XPS) scans, using the same beam line, showed no discernible impurities, with a detection sensitivity of a few percent of a monolayer. After 12 h in ultrahigh vacuum (UHV) only a few percent of a monolayer of O and C, as calibrated by deliberate 0.05 L (1 L $= 10^{-6}$ Torr s) exposures, appeared in the XPS scans, with small changes in the valence band and $4f$ regions. Oxygen appeared as O_2 on the surface, as judged by the O $1s$ peak, and the changes at low binding energy were a small peak growing around 5 eV and the filling in of the minimum at 6.5 eV. That undetected impurities cause the spectral difference is unlikely. Hydrogen is the most likely, since it dominates the residual gas in UHV chambers and at low levels it could not be detected by any spectroscopy we used. Evaporation of Eu in 10^{-8} Torr of H_2 resulted in spectra like those of Fig. 2. (See also the discussion of plasmons below.)

The peak at 2.3 eV in Figs. 1 (solid curve) and 2 arises from the $4f$ electrons. It increases in intensity as the photon energy rises above 25 eV, then diminishes rapidly at 130 eV, just before the $4d \rightarrow 4f$ excitation threshold, thereby following the energy dependence of the $4f$ excitation cross section. It exhibits a resonance as the photon energy passes through the $4d \rightarrow 4f$ resonance. The FWHM of this peak is 1.5 eV, and its shape does not change as the photon energy changes, indicating that there is apparently no unresolved structure due to a bulk and surface component.

The peak at 4.7 eV varies in intensity as the photon energy varies, as expected from the $5d$ electrons, but relativistic band calculations for bcc Eu show no bands deeper than 3.6 eV. In fact all calculations to date place the occupied $5d$ states above the $4f$ states, so the assignment of this peak to $5d$ electrons cannot yet be made. The weak structure in the secondary electron spectrum around 10 eV shows a resonance at the threshold for the $4d \rightarrow 4f$ excitations. The spectra for metallic Eu (Fig. 1, dashed) are quite different. There is a clear Fermi edge, and the double peak has components whose intensities vary with photon energy (and electron kinetic energy). These peaks were attributed by Gerken *et al.* to the $4f$ bulk and surface levels [2]. The spectra were decomposed into two components, each being a set of the several lines expected from the atomic calculation of the $4f^7 \rightarrow 4f^6$ ionization, each convolved with a Doniach-Sunjic line shape. Then the two sets were weighted by the surface/volume ratio and separated by a surface binding energy shift of 0.6 eV. The fit was excellent, and the result is physically reasonable. Similar spectra were found with lower resolution in XPS.

Spectra like those of Fig. 2 were generally found for thicknesses under about 100 Å. Films thicker than about 200 Å always give spectra like the dashed one in Fig. 1. Intermediate thickness gave a mixed spectrum that evolved toward that of metallic Eu (Fig. 1, dashed) with time. Thus we appear to have a metastable phase of Eu, one that is not metallic and which exists only in thin film form, but at coverages up to tens of monolayers. We note that insulating films of divalent, normally metallic elements have been found previously, e.g., Hg on Cu(100) [10], Hg on W(110) [11], but such films were insulating only at coverages no larger than a monolayer. Studies of such *thin* nonconducting films of metal atoms on metals have been reviewed [12].

The photoelectron spectra on polycrystalline substrates have been duplicated for thinner layers grown with orientational epitaxy on single crystal substrates. Monolayer Eu films were deposited on single crystal Ta(110) substrates at 300 K. A hexagonal LEED pattern appeared at coverages above about 0.4 monolayer [ML in Ta(110) density units] with a row of spots along the Ta 100 direction (Fig. 3). The pattern expanded with coverage until the monolayer was complete at a coverage of 0.53. The nearest neighbor distance a_0 shrank from 4.56 to 4.09 Å during this stage. As the thickness increased beyond 1 ML the hexagonal pattern expanded reaching 4.59 Å at 3 ML, rotated a few degrees away from its original alignment, and exhibited a doubling of the spots. For bcc Eu, $a = 3.97$ Å, so, at least in two dimensions, this Eu

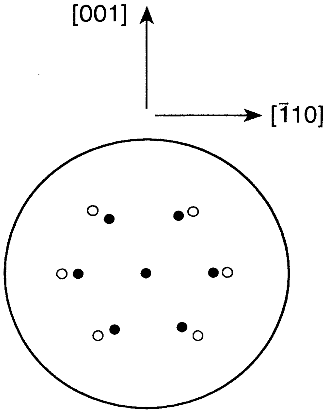

FIG. 3. Schematic LEED pattern from a 10 Å film of Eu on Ta(110). The open circles represent the spots from the Ta substrate, observed only for lesser coverages.

overlayer is expanded with respect to bcc Eu, as predicted for fcc Eu [13]. Orientationally epitaxy was retained at larger thicknesses, but the substrate spots, used for calibration, disappeared. However, a_0 did not change much with additional coverage. When the thickness of the films reached about 50 Å, the hexagonal pattern gradually disappeared and a pattern due to bcc (110) domains appeared, finally reaching a single-domain pattern oriented with the same axes as those of the underlying Ta, but with the nearest neighbor spacing of bcc Eu, incommensurate with that of Ta. The film structures change with thickness and annealing. These changes will be discussed elsewhere [5].

Photoelectron spectra of a close-packed film a few monolayers thick, taken at resonance to reduce the substrate contributions, resemble the solid curve in Fig. 1. Thus the new nonmetallic phase of Eu has a threefold or sixfold rotational axis normal to the Ta(110) surface, and fcc is one of several possible structures for multimonolayer films. The three-dimensional structure is not known, and LEED I-V analysis does not appear promising unless the quality of the films can be improved, for the LEED patterns are sharp over only a small range of electron beam energy.

There have been other studies of fcc epitaxial layers on bcc 110 substrates. A model for orientational epitaxy was first developed by Novaco and McTague [14]. References [15] and [16] summarize previous work on such systems. This work and calculations with simple two-body force models, and experiments, show that when the ratio of bulk lattice parameters, fcc overlayer material/bcc substrate is near 1.16 or 1.33, an energy minimum is reached with an angular misorientation of about 0° and 5°, respectively, and the Kurdjumov-Sachs (KS) and Nishiyama-Wasserman (NW) orientations, respectively. We note that the lattice parameter ratio for Eu on Ta, 1.75, if bulk "fcc" Eu has the same atomic density as bcc Eu, is beyond the range considered in the calculations. Our close-packed Eu films started with the NW orientation, but switched to KS as they grew thicker. Grey and Bohr [17–19] have discussed an alternate picture which permits stable orientational epitaxy on incommensurate overlayers, one based on the existence of finite domains which allow a minimization of any periodic interaction energy.

Skriver [13] calculated the total energy of Eu at 0 K as a function of volume for several assumed crystal structures. He found that for an atomic volume larger than that of the normal bcc phase, an fcc phase is more stable. Moreover, this phase is a semimetal or semiconductor [20], as might be expected for a divalent element. A nonrelativistic calculation will not give a gap around the Fermi level for such a situation, but the nonmetallic nature of this phase is attained in a fully relativistic calculation when spin-orbit coupling opens a gap in two bands which would otherwise cross at the Fermi level [21]. This phase can account for a number of our observations. The Fermi level should be in the gap, or in a region of very small density of states. In fact, in a search for it in the EDC of this phase, using a very low photon energy to enhance the cross section and allowing use of a LiF filter to eliminate the higher-order background, we found a Fermi edge no larger than 1% that of bcc Eu.

The calculated density of states for fcc Eu with the same Wigner-Seitz radius as for the bcc phase [20] has a small gap at the Fermi level, in contrast to that for the bcc phase. The differences below the Fermi energy occur only in the first 1.5 eV, but this is the only region free of strong $4f$ structure in the EDCs. The first 0.5 eV or so of this region may change in relativistic calculations.

The electron energy loss spectrum was measured in reflection on both phases of Eu. Not considering the $4f$ electrons, the calculated free electron plasmon energy, $h\omega_p$, for Eu is 7.58 eV, while that for $\mathrm{EuH_2}$ is 11.37 eV. A peak in the loss spectrum at about 7 eV has been attributed to the volume plasmon [22,23]. Using an 800 eV primary beam, we find a broad loss peak at 7.34 eV in metallic Eu. The loss spectrum for the new phase of Eu is very similar, with a shift of the plasmon peak to 7.50 eV. This shift implies a 4.4% higher density electron gas for the new phase, assuming free-electron-like behavior [24]. These measurements were made on a rather thick polycrystalline film, for which the density in the plane is lower than that of bulk Eu (see below). Assuming the spacing normal to the surface is not inordinately small, a lower electron density is expected. On the other hand, the new phase is not metallic, hence has a band gap E_G. In such a case, for a simple model the observed plasmon energy is given by $[(h\omega_p)^2 + (E_G)^2]^{1/2}$ [25,26]. Assuming $h\omega_p$ is the same for both phases, E_G is 1.54 eV, close to the minimum gap one would get from the photoemission data.

Resistance measurements taken during presumably polycrystalline Eu film growth on single-crystal sapphire substrates [5] confirm that the films grow continuously once a percolation threshold is reached. As the thickness grows the resistivity decreases (Fig. 4) with an "arrest" at about 1 ML, lasting until about 3 ML, after which it drops more rapidly. The resistivity in this arrest is 3–10 times that of bulk Eu. If growth is stopped at about 1 ML and the temperature increased, the resistivity falls. This was followed by a more complex behavior, increasing resistivity with increasing temperature, culminating in one or more evaporative loss stages. If the growth is stopped at about 7 ML, in the bcc phase, the resistivity is nearly independent of temperature. At about 1 ML, Arrhenius plots give different activation energies, from 25 meV to over 1 eV, dependent on evaporation rates. More extensive work, now ongoing, is needed to determine the nature of conduction in this new phase: intrinsic conduction and a small gap or ionization of impurities or defects. Annealing effects may also play a role in the temperature dependence. Although charging prevented LEED studies from being attempted, the shape of Fig. 4 suggests that the sample phases form on sapphires as on Ta or W.

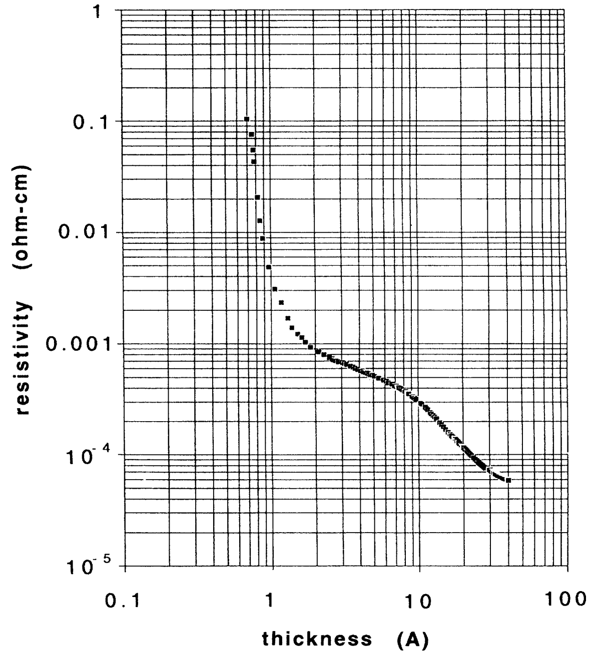

FIG. 4. Resistivity of a film of Eu on sapphire at 300 K vs film thickness. The resistivity has been obtained from the resistance using only the thickness measured by a quartz oscillator, not the unknown actual thickness. As the thickness increases, the in-plane lattice parameter changes, contributing to the slope of the "plateau." The bulk resistivity of bcc Eu is 10^{-4} Ω cm at 300 K.

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[1] R. Kammerer, J. Barth, F. Gerken, A. Flodstrom, and L. I. Johansson, Solid State Commun. **41**, 435 (1982).
[2] F. Gerken, A. S. Flodstrom, J. Barth, L. I. Johansson, and C. Kunz, Phys. Scr. **32**, 43 (1985).
[3] F. Gerken, J. Phys. F **13**, 703 (1983).
[4] C. G. Olson, Nucl. Instrum. Methods Phys. Res., Sect. A **266**, 205 (1988).
[5] C. G. Olson, X. Wu, and D. W. Lynch (to be published).
[6] U. Becker, H. G. Kerkhoff, D. W. Lindle, P. H. Kobrin, T. A. Ferrett, P. A. Heimann, C. M. Truesdale, and D. A. Shirley, Phys. Rev. A **34**, 2858 (1986).
[7] W. H. Hocking and J. A. D. Matthew, J. Phys. C **21**, L403 (1988).
[8] M. Richter, M. Meyer, M. Pahler, T. Prescher, E. v. Raven, B. Sonntag, and H.-W. Wetzel, Phys. Rev. A **40**, 7007 (1989).
[9] O. P. Sairanen and S. Aksela, J. Phys. Condens. Matter **4**, 3337 (1992).
[10] P. A. Dowben, D. LaGraffe, D. Li, G. Vidali, L. Zhang, L. Dottl, and M. Onellion, Phys. Rev. B **43**, 10677 (1991).
[11] J. Zhang, D. Li, and P. A. Dowben, J. Phys. Condens. Matter **6**, 33 (1994).
[12] E. W. Plummer and P. A. Dowben, Prog. Surf. Sci. **42**, 201 (1993).
[13] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).
[14] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. **38**, 1286 (1977).
[15] R. Ramirez, A. Rahman, and I. K. Schuller, Phys. Rev. B **30**, 6208 (1984).
[16] E. Bauer and J. H. van der Merwe, Phys. Rev. B **33**, 3657 (1986).
[17] F. Grey and J. Bohr, in *Phase Transitions in Surface Films 2,* edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain (Plenum Press, New York, 1991), p. 83.
[18] F. Grey and J. Bohr, Europhys. Lett. **18**, 717 (1992).
[19] F. Grey and J. Bohr, Appl. Surf. Sci. **65/66**, 35 (1993).
[20] H. L. Skriver (private communication).
[21] B. N. Harmon (private communication).
[22] F. P. Netzer, G. Strasser, G. Rosina, and J. A. D. Matthew, Surf. Sci. **152/153**, 757 (1985).
[23] J. Kolaczkiewicz and E. Bauer, Surf. Sci, **265**, 39 (1992).
[24] J. G. Endriz and W. E. Spicer, Phys. Rev. B **2**, 1466 (1970).
[25] C. Horie, Prog. Theor. Phys. **21**, 113 (1959).
[26] T. Miyakawa, J. Phys. Soc. Jpn **24**, 768 (1968).