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Strain-modulated reflectivity of lutetium

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We report strain-modulated-reflectivity measurements on lutetium in the energy range 1.5–6 eV. In order to avoid the effects of oxidation, the measurements were performed in an UHV chamber on polycrystalline films deposited *in situ* onto a quartz-crystal strain transducer. Measurements taken with light polarized parallel and perpendicular to the major strain axis of the transducer have been analyzed to obtain the hydrostatic-strain derivative of the dielectric function by using an isotropic approximation. Several critical-point structures can be identified, and the average deformation potential for *sp*- to *d*-band transitions is measured to be -6 eV per unit hydrostatic strain. The results show general agreement with calculated band structures.

INTRODUCTION

The strain dependence of the electronic band structure of lutetium is of interest because of its influence on the superconducting transition temperature and on the series of equilibrium crystal structures adopted at high pressures.[1,2] The understanding of this influence relies at present on calculated band structures. In this paper we report measurements of strain-modulated band-structure measurements on this material.

Lu is at the end of the rare-earth series of the Periodic Table, and with its filled $4f$ shell and three $(5d^1 6s^2)$ outer electrons it is often described as closely resembling a transition metal. A number of band structure calculations have been reported since the first effort of Keeton and Loucks[1–4] and there is general qualitative agreement among them, except for the precise position of the filled $4f$ levels. Photoelectron measurements place these levels about 6 eV below the Fermi level E_F.[5] The general picture then for the states within a few electron volts of the Fermi energy is that they are relatively flat and of predominantly *s*, *p*, and *d* character, filled in approximately equal weights.

Static optical measurements normally provide a convenient way of probing the states within a few electron volts of E_F, but the reactivity of the rare-earth metals has lead to discrepancies between previous measurements. In addition, the optical properties have proved rather difficult to interpret due to an overabundance of optical transitions between the flat bands, leading to a somewhat structureless optical conductivity. Thus although general features can be identified, individual optical transitions cannot. With this in mind we have performed optical reflectivity and piezoreflectivity measurements on lutetium, and we find that the strain-modulation information permits both the identification of individual features and a direct measurement of an average deformation potential than can be compared with the calculated pressure dependence of the band structure.

EXPERIMENTAL DETAILS

The rare-earth metals oxidize rapidly in the presence of air, so we have performed our measurements on films of lutetium prepared *in situ* in an UHV system with a base pressure of 10^{-10} Torr. Although the pressure rose during the evaporation of the films, the net dose was no more than a few langmuirs (1 $\mathrm{L} \equiv 10^{-6}$ Torr sec), so that no more than one monolayer of oxide will have formed. From studies of the changes in the optical properties after controlled exposure to oxygen, which will be published at a later date, exposures of at least 10^4 L are required before the effects are noticeable. We are thus confident that we have measured the optical properties of clean polycrystalline films of lutetium.

The films were deposited on polished single crystals of quartz, of dimensions $4 \times 4 \times 115$ mm^3 and of $-18.5°$ *X* cut, which permits the piezoelectric excitation of a longitudinal acoustic wave in the rod.[6] For the piezoreflectance measurements these crystals were excited in the third longitudinal vibrational mode at a frequency of 66.67 kHz, using the outer thirds of the length as drive and gauge components.[7,8] The samples were deposited at the strain antinode in the center of the crystal. The longitudinal strain amplitude was determined from the voltage developed between contacts deposited on the gauge end of the rod,[7] and the transverse strain on the sample surface could then be calculated from the elastic constants of quartz.[6] The third diagonal component of the strain tensor in the sample was determined by treating the polycrystalline film as isotropic, assuming that the stiffness tensor was given by a weighted average over the values for crystallites oriented with their *c* axes parallel and perpendicular to the film surface.[9,10]

Reflectivity and piezoreflectivity measurements were performed using the *VW* configuration.[11] Monochromatic light of polarization either parallel or perpendicular to the long axis of the quartz rod was provided by use of a quartz pile-of-plates polarizer and a Jobin Yvon 10-cm double monochromator. The light was detected with a photomultiplier tube, and in the piezoreflectance mode the supply voltage was controlled to keep the average current at a predetermined level, thus generating directly the relative strain modulation of the reflectivity, $(\Delta R/R)$.[8]

Kramers-Kronig (KK) analysis was performed on the data to determine the dielectric function (ϵ_1,ϵ_2) and its strain derivative for both polarizations relative to the strain axis. The assumption of isotropy (except, of course, for the induced strain) then permits the optical response for a hydrostatic strain to be determined from the responses for the two polarizations.[12] We center our discussion below on this hydrostatic strain response, which can be compared directly to band structure calculations.[2]

RESULTS AND DISCUSSION

The reflectivity of the lutetium films is shown in Fig. 1(a), where it is also compared with two earlier sets of results.[13,14] The level of agreement is typical of that seen in this field, and the small discrepancies are almost certainly related to the presence of oxide layers in earlier work. After KK transformation we find the optical estimate $[(\hbar\omega)^2\epsilon_2]$ of the joint density of states (JDOS) that is displayed in Fig. 1(b). The peak in this parameter centered on 2.5 eV is similar to that seen in the closely related material gadolinium,[15] and is generally believed to arise from optical transitions from *sp*-like bands just below E_F to *d*-like bands centered about 1.3 eV above E_F.[1-4,15] The transitions above 4 eV involve higher energy final states.

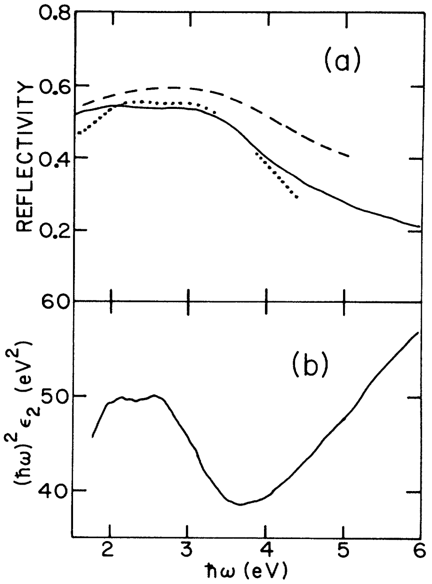

FIG. 1. (a) Reflectivity of lutetium compared with earlier measurements by Schüler (Ref. 13, dashed line) and a weighted average of the single crystal data of Weaver and Lynch (Ref. 14, dotted line). (b) Optical joint density of states for lutetium.

In Fig. 2 we show the strain derivative of the optical JDOS for hydrostatic strain, and compare it with the suitably scaled version of the energy derivative of the static JDOS of Fig. 1(b). There is a remarkable similarity between the two curves, which immediately suggests that the overall weight of the *sp* bands moves toward the *d* bands under extensive hydrostatic strain with an average deformation potential of −6 eV per unit strain. This deformation potential is in agreement with the predicted pressure dependence of the band structure of lutetium.[2]

The conclusion that the *sp* and *d* bands converge under extensive strain would seem at first sight to be at variance with the result, determined from the same band-structure calculations, that weight is shifted from the *sp* to the *d* bands under pressure (compressive strain).[1,2] The apparent disagreement is, however, eliminated by noting that there is a branch of the *sp* band, along the hexagonal face near the *M* point, that shifts up in energy with pressure, against the trend.[2] This branch lies very close to the Fermi energy, and it thus depopulates under pressure. This part of the band provides the initial state for transitions into the *d* band at about 2 eV above E_F, and accounts for the peak near 2 eV in the piezo-signal of Fig. 2. A fit to both the real and the imaginary parts of the strain-modulated signal, together with the theoretical knowledge of the curvatures of the initial- and final-state bands, can be used to determine the energy of the transition responsible for this peak and the sign of its deformation potential.[12,16] We find that the energy of the critical point transition at *M* is 2.3 eV, compared with the predicted energy for 2.08 eV, and that the hydrostatic deformation potential is positive. In this case the magnitude of the deformation potential cannot be determined, for the feature cannot be seen in the unstrained reflectivity.

Table I lists two further features in the piezoreflectance that we have identified with critical point transitions in the calculated band structure of lutetium. The assignments have been made by first establishing the energy and character of the feature in the hydrostatic strain-modulated signal, and then looking for an allowed transition in the band-structure calculations which had the curvatures and deformation potential sign that corresponds to the observed signal. Note that in one case there are two alternative assignments.

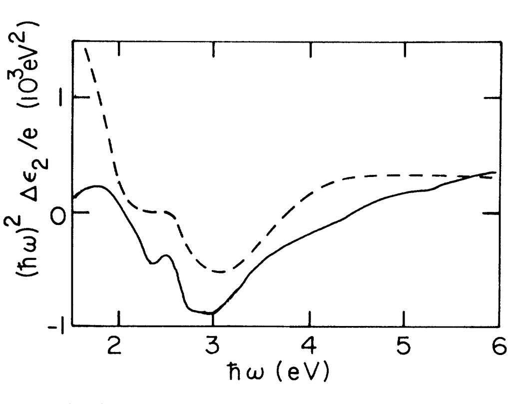

FIG. 2. The hydrostatic strain derivative of the optical joint density of states compared with the energy derivative of Fig. 1(b), multiplied by 6 eV (dashed line).

TABLE I. Features identified in the hydrostatic strain signal, labeled with the energy gap, broadening parameters, and transition type. Also given are the tentative transition assignments with their calculated energy from the band structure of Ref. 1. Rows η and type M_i are defined in Ref. 16.

Energy gap E_g (eV)	2.08	2.20	2.67
Broadening parameter η (eV^{-1})	0.22	0.16	0.11
Type of critical point transition	M_0 or $-M_2$	M_3 or $-M_1$	M_0 or $-M_2$
Transition assigned (with calculated energy)	$M_1^+ \rightarrow M_4^-$ (M_0) 2.32 eV	$M_3^+ \rightarrow M_1^-$ (M_1) 2.01 eV or $L_1 \rightarrow L_1$ (M_1) 2.16 eV	$M_3^+ \rightarrow M_4^-$ (M_2) 2.80 eV

CONCLUSIONS

We have reported measurements of the strain-modulated optical constants of lutetium. Special care has been exercised to ensure that the oxide layer on the sample was sufficiently thin that the data represent the response of the pure metal. We have determined the hydrostatic response of lutetium from polarized piezoreflectivity data on our polycrystalline samples. Three individual critical-point transitions can be seen in the results, and their position and the signs of their deformation potentials can be understood with reference to band-structure calculations. The general behavior of the hydrostatic response indicates that the *sp* and *d* bands converge under expansive strain and the magnitude and sign of the deformation potential for the overall *sp*- to *d*-band separation has been determined, and is in agreement with the calculated value.

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