

(B1) are the same as before, but the eigenvalues are not $\{(N + \frac{1}{2})\hbar\Omega' - m\hbar[\frac{1}{2}(\Omega' - \Omega)]\}$. The coherent states are also the same as before except that both α and ξ will depend on time. Thus

$$\alpha(t) = \alpha(0) \exp[-i[\frac{1}{2}(\Omega' + \Omega)]t],$$

$$\xi(t) = \xi(0) \exp[-i[\frac{1}{2}(\Omega' - \Omega)]t].$$

The wave packet will therefore follow the classical motion.

To calculate Z_{\perp} in this case, one may take all the limits of integration from 0 to ∞ . The parti-

tion function is then

$$Z_{\perp} = \left(4 \sinh \frac{\hbar(\Omega' - \Omega)}{4kT} \sinh \frac{\hbar(\Omega' + \Omega)}{4kT} \right)^{-1}.$$

For $\omega_0 \ll \Omega$, Z_{\perp} becomes

$$Z_{\perp} = \left(\frac{2\hbar\omega_0^2}{kT\Omega} \sinh \frac{\hbar\Omega}{2kT} \right)^{-1}.$$

Except for a proportionality constant, this equation is the same as Eq. (4.8) and therefore leads to the same magnetization and susceptibility.

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Spin-Polarized Energy Bands in Eu Chalcogenides by the Augmented-Plane-Wave Method

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Spin-polarized energy bands in the Eu chalcogenides have been obtained by the augmented-plane-wave (APW) method. The $4f$ band positions are extremely sensitive to the exchange potential used. A reduced exchange parameter of $\frac{3}{4}$ for the magnetic Eu^{2+} ions has produced proper energy gaps and relative f band positions for EuO , EuS , and EuSe . We have obtained the $f(t)$ bandwidth as about 0.5 eV and the up- and down-spin f band separation as about 6 eV. We have also obtained anion p bandwidths of about 2 eV which are almost constant for the Eu chalcogenides. The calculated density of states agrees qualitatively with photoemission data, except for the experimental density of states of the $4f(t)$ band which has a large bandwidth of about 1.5 eV. The probable causes of this discrepancy are multiple scattering of the $4f$ electrons with phonons and electrons, or recombinations with Eu^{3+} ions. The observed absorption-edge red shifts are due to the spin-polarized exchange splitting ΔE_{ex} of the lowest conduction band X_3 . Estimated ΔE_{ex} values are 0.4-0.5 eV for Gd metal and Eu chalcogenides. The $f(t)$ bands in Eu and Gd metals are expected to be located within 3 eV below the Fermi level. The high-energy reflectivity data, effective masses, possible conduction mechanism, and APW charge analysis have been discussed.

I. INTRODUCTION

Recently an increasing number of authors have studied the Eu chalcogenides, both experimentally

and theoretically. Eu chalcogenides have a simple NaCl structure and are magnetic semiconductors. Despite extensive studies of the rare-earth mate-

rials, we know little about the f electrons which are responsible for peculiar physical properties. Several authors^{1,2} have studied theoretically the energy bands in the rare-earth elements. However, they have found it difficult to locate the f band positions properly because of its sensitive dependence on the exchange potential used. It is an equally difficult problem to identify and locate the f bands experimentally. Various impurities in the rare-earth substances often cause unpredictable results.

Müller³ has studied room temperature reflectivity and transmission for Eu and Ba metals (up to 4 eV), which have isoelectronic structures. He has found almost identical optical behavior for Eu and Ba metals, and has concluded that the $4f$ electrons do not influence the optical spectrum, and that the $4f$ levels might be located far below the Fermi level. Schüler⁴ has studied temperature-dependent transmission of Gd and Lu thin films, from which he has found that the transmission maximum of Lu is located at 0.75 eV which is independent of temperature. The transmission maximum of Gd is located at 0.6 eV at room temperature and is split into two peaks below the Curie temperature T_C , at ~ 0.8 and 0.45 eV, respectively. The extra peak is due to the spin-polarized exchange splitting of the bands, which is estimated to be about 0.4 eV for Gd. However, he has not obtained any information on the possible f band positions. Blodgett *et al.*⁵ have measured photoemission (UPS) for Gd, and reported that a possible $f(\uparrow)$ band location is about 6 eV below the Fermi level E_F with a work function of 3.1 eV, and that the possible exchange splitting ΔE_{ex} is less than 0.1 eV from their temperature-dependent photoemission measurements.

In this work, we report the magnetic energy bands in EuO, EuS, and EuSe obtained by the augmented-plane-wave (APW) method, and their relationship to the various experimental results. Methfessel and Mattis⁶ have made a complete up-to-date review of work on the Eu chalcogenides.

II. EXCHANGE POTENTIAL

Most of the first-principle energy band calculations for solids have been based on the Slater $\rho^{1/3}$ exchange potential⁷ deduced from a free-electron model. Recently several authors⁸⁻¹⁰ have studied this $\rho^{1/3}$ exchange potential. The original $\rho^{1/3}$ exchange potential has led to incorrect results for the f band positions in our previous magnetic energy bands in EuS by the APW method.¹¹ For this reason, we reexamine the energy band calculations, with particular regard to the exchange potential problem in the Eu chalcogenides. The procedures have been discussed

in our previous paper.¹¹

We write the reduced crystal exchange potential

$$V \pm \frac{n}{ex}(r) = -6 \left(\frac{3}{8\pi} \right)^{1/3} \{ A_n^3 [\rho_t^n(r) \pm B_n \rho_s^n(r)] + \sum_m N_m A_m^3 \langle \rho_t^m(r) \pm B_m \rho_s^m(r) \rangle \}^{1/3}, \quad (1)$$

where A_n and B_n are the exchange parameters for the n -type atoms, n is the index of the atoms in the solid, ρ_t^n and ρ_s^n are total and spin densities, respectively, for the n -type atoms, N_m is the number of atoms in the m th shell, and in $\langle \rangle$ are the spherically averaged values. In our study of the Eu chalcogenides, A_1 and B_1 stand for the negative ions, O^{2-} , S^{2-} , and Se^{2-} , and A_2 and B_2 for the positive Eu^{2+} ion.

Figure 1(a) shows a series of test results for the spin-polarized energy bands in EuS where $A_1 = A_2$ is varied from 1 to $\frac{2}{3}$ with $B_1 = B_2 = 1$. Here only the energy bands of main interest in this study are shown. All of these are for up-spin electrons except for the down-spin f bands. As one can see from this figure all energy bands shift upwards with decreasing exchange potential, although the relative spacings for the s band Γ_1 , the p bands L_1 , X'_5 and Γ_{15} , and the d bands X_3 , Γ'_{25} and Γ_{12} are almost unchanged. Nevertheless, the forbidden energy gap between the anion p band Γ_{15} and $5d$ band X_3 becomes smaller on reducing the exchange potential. Similar calculations for EuO and EuSe indicate the same behavior. These studies show that the forbidden energy gap between the valence band p Γ_{15} and the conduction $5d$ band X_3 decreases on going from EuO to EuS and EuSe, contrasting with experimentally observed changes in the opposite direction.¹² These results suggest that the anion and magnetic cation do not obey the same reduced exchange parameters.

Figure 1(b) shows the series of test results with $B_1 = B_2 = A_1 = 1$ and A_2 varying from 1 to $\frac{2}{3}$ for EuO. Similar results are also obtained for EuS and EuSe. One can see from this figure that the up-spin f bands do cross the valence p bands, Γ_{15} and X'_5 , at $A_2 = 0.825$, and stay between these p bands and the conduction $5d$ band X_3 for A_2 values down to 0.713. In this region the valence p bands Γ_{15} and X'_5 , and the conduction $5d$ band X_3 are farther from each other because of the f - p hybridization due to the f - p admixing, as will be discussed later. The bottoms of the p band L_1 and the conduction s band Γ_1 remain unchanged. The conduction $5d$ bands Γ'_{25} and Γ_{12} slowly increase in energy on reducing the exchange potential. A value of $A_2 = \frac{3}{4}$ yields energy gaps of 1.12 eV for EuO, 1.65 eV for EuS, and 1.78 eV for EuSe, between the valence $f(\uparrow)$ band and the conduction d band X_3 , values which are in good agreement with

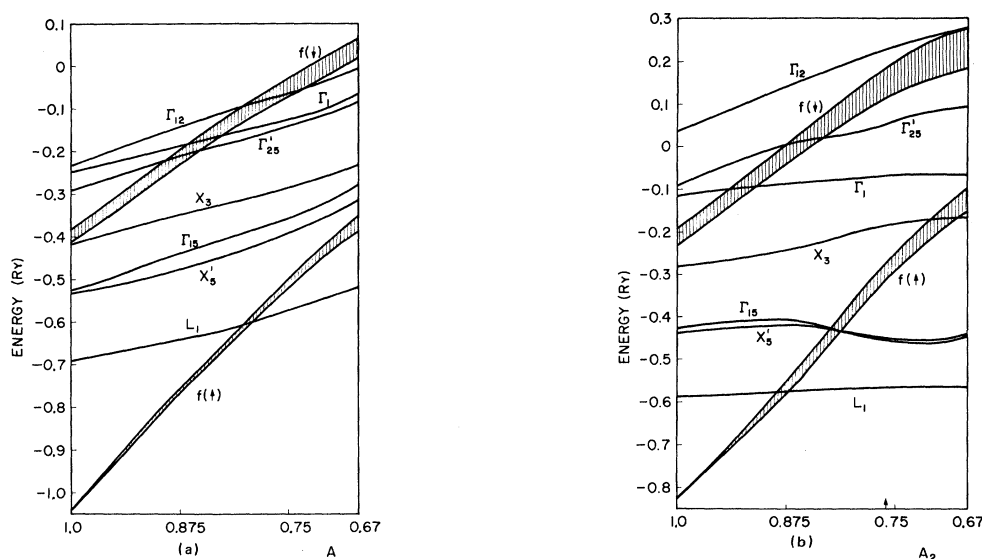


FIG. 1. Energy bands versus the reduced exchange parameters: (a) for EuS ($A_1=A_2=A$, $B_1=B_2=1$) and (b) for EuO as a function of A_2 ($A_1=B_1=B_2=1$).

the experimental data.¹² These results indicate that the top of the valence band is the up-spin $f(\uparrow)$ band instead of the p band as reported before, and the bottom of the conduction band is the $5d$ band X_3 which has been obtained in our previous work.¹¹

From the energy band point of view an occupied energy band in the k space for a given electron is more atomlike considerably below the Fermi level, and becomes broader approaching the Fermi level. Figures 1(a) and 1(b) show that the $f(\uparrow)$ bands behave in this manner and become broader approaching the Fermi level, although the f bands are much more localized than the s , p , and d bands. In the case of the Eu chalcogenides, the $f(\uparrow)$ bands are the highest valence bands, and have a finite bandwidth.

The preliminary test results also indicate that the two-parameter reduced exchange potential with $A_1=A_2=A$ and $B_1=B_2=B$ does not produce proper energy gaps for the Eu chalcogenides for various combinations of A and B values.

It is worth noting that the APW sphere radius for Eu^{2+} decreases almost linearly with decreasing exchange potential while that of the anion increases in the same manner.

III. ENERGY BAND CALCULATIONS

Figures 2–4 show the spin-polarized energy bands in EuO, EuS, and EuSe, respectively, which have been obtained by the APW method using the reduced exchange parameter $A_1=B_1=B_2=1$ and $A_2=\frac{3}{4}$ discussed before. As we can see from these figures the over-all energy bands are simi-

lar among these Eu chalcogenides. The main differences between present results and the results ($A_1=A_2=B_1=B_2=1$) have been discussed in our previous paper.¹³

The up- and down-spin f band separation is about 6.0 eV which is almost constant for all Eu chalcogenides (the free-atomic value is about 7.8 eV¹⁴). It takes about 6.0 eV to make an internal spin flip of the $f(\uparrow)$ electrons. Therefore direct spin-flip transitions from the $f(\uparrow)$ electrons to other conduction bands cannot be expected at least up to 7 eV.¹⁵ The $f(\uparrow)$ bands are located in between the anion p band Γ_{15} and the conduction $5d$ band X_3 . This is the first work to clearly show that the $f(\uparrow)$ bands are the highest valence bands. Methfessel¹⁶ was the first one to point out the possibility of $f(\uparrow)$ bands as the highest valence bands, based on the fact that the large abnormal effects observed in various experiments could not be produced unless we assume such a situation. In Figs. 2–4 the down-spin $f(\downarrow)$ band positions are indicated at the zone center Γ , and are considerably intermixed with the rest of the overlapping s , p , and d bands everywhere in the Brillouin zone.

The energy differences between Γ_{12} and Γ'_{25} are given in Table I, which are equivalent to the $10Dq$ values. Methfessel *et al.*¹⁷ have assumed $10Dq$ values as energy differences between the first and the second major reflectance peaks at room temperature, which are 3.2 eV (EuO), 2.2 eV (EuS), and 1.88 eV (EuSe) (see Table IX). Their tentative assignments for the $10Dq$ values are close to

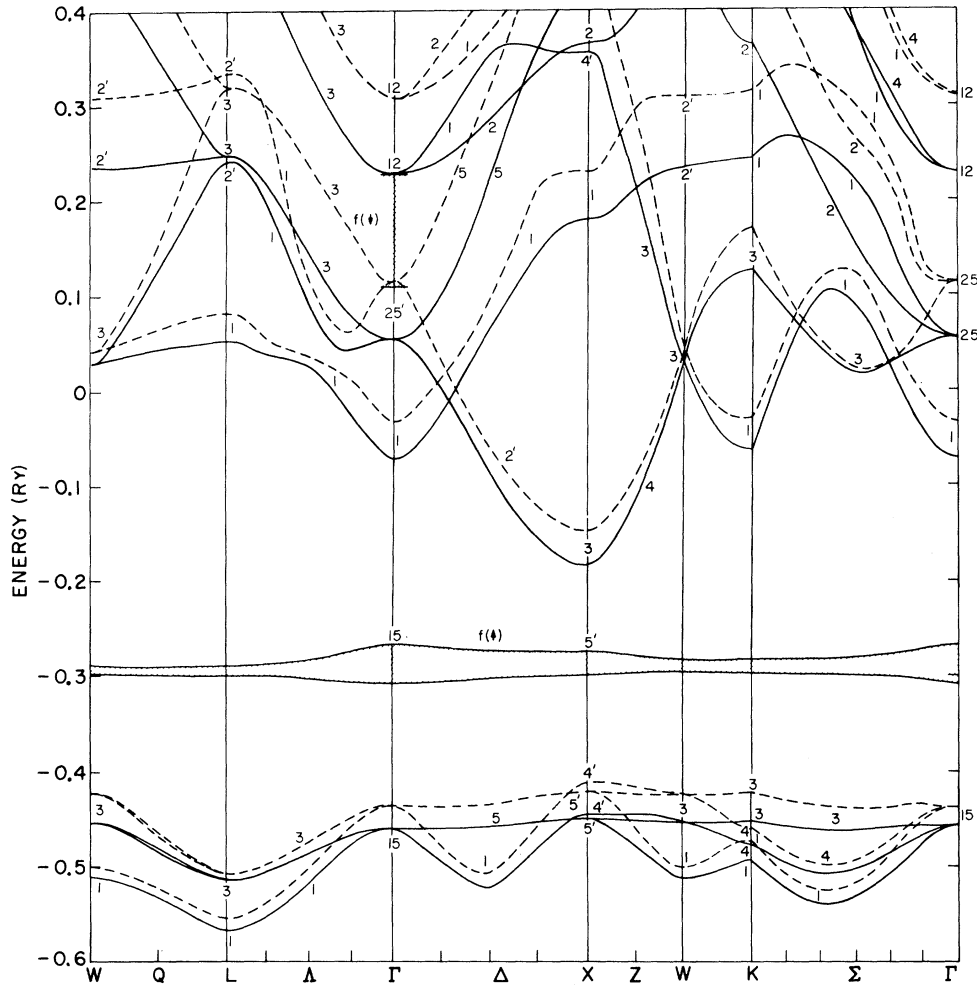


FIG. 2. Energy bands for EuO. Solid lines for the up-spin electrons and dashed lines for the down-spin electrons.

the maximum values of $\Gamma_{12} - \Gamma_{25}'$. However, the first reflectance peak is an interband transition from $f(\uparrow)$ bands to X_3 and not to $\Gamma_{25}'(t_{2g})$, and the second major peak might originate mainly from the anion p band as will be discussed later. The energy separations between the $f(\uparrow)$ bands and the anion p bands decrease from EuO, EuS to EuSe (see Table VI). In the case of EuSe (Fig. 4) the anion p band is actually overlapped somewhat with the $f(\uparrow)$ bands, and we could expect that there will be a delicate f - p separation at the zone center depending on the spin structures. In the case of EuTe, it might be the case that the p band Γ_{15} is slightly higher than the $f(\uparrow)$ bands at the zone center.

Some of the APW charge analysis obtained in our work is shown in Tables II–IV. The conduction s band Γ_1 has a large admixture of the $6s$ -like of Eu^{2+} and the s -like of the anion. The amount of the anion s -like intermixing increases from EuO, EuS to EuSe due to an increasing anion size. About

67% of the charge is outside of the APW spheres which are expected to be mostly $6s$ -like. The large amount of the anion s -like admixture to the Γ_1 is due to the loosely bound two extra p electrons of the anion, which are expected to be easily excited to the conduction s band Γ_1 . We have also studied the spin-independent part of the relativistic effects at Γ and X points. The energy difference between $\Gamma_1 - X_3$ for EuS is about 1.7 eV and becomes about 1.2 eV with relativistic effects. In the case of the EuO the value of $\Gamma_1 - X_3$ is about 1.5 eV, which becomes about 0.5 eV when we include the relativistic effects. Therefore, the conduction bands X_3 and Γ_1 for EuO should be at almost the same energy, although the s band Γ_1 becomes noticeably higher than X_3 for EuS and EuSe. However, in our studies we have neglected the non-muffin-tin terms. Such effects have been previously studied for KCl^{10} and ReO_3 .¹⁸ The influence of the non-muffin-tin terms on the $6s$ and the center of gravity of the $5d$ bands is reported to be a relative

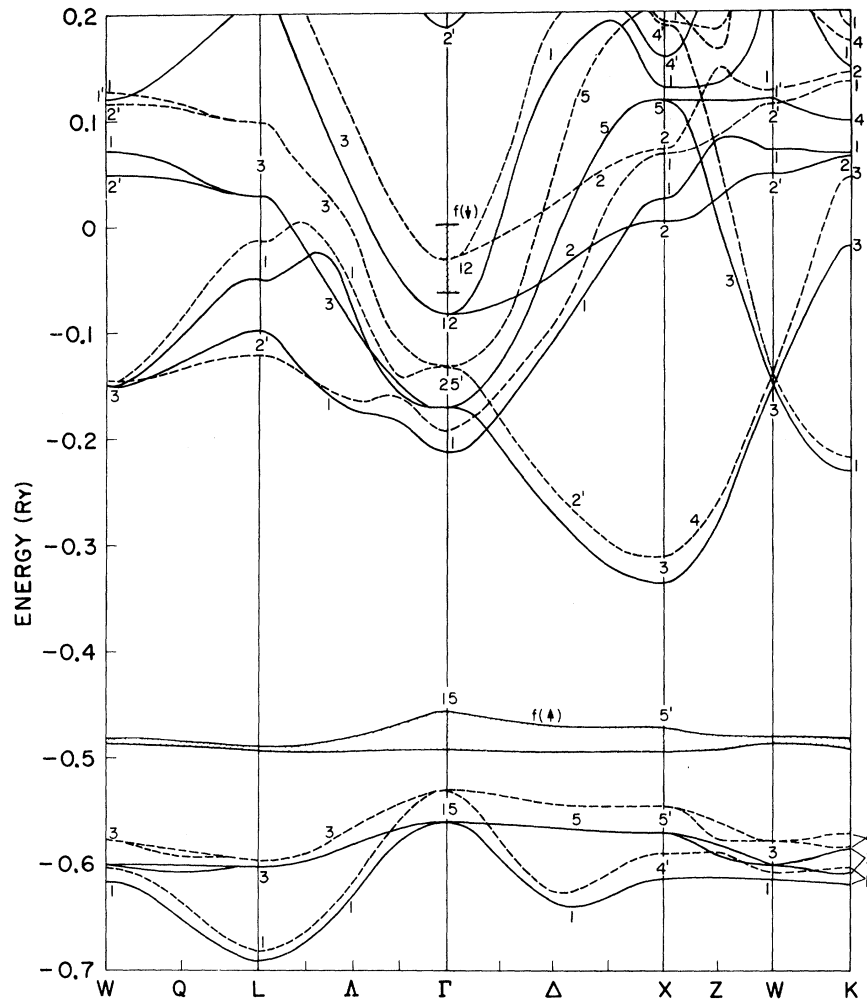


FIG. 3. Energy bands for EuS. Solid lines for up-spin electrons and dashed for the down-spin electrons.

shifting muffin-tin value of order 0.25 Ry for ReO_3 in the opposite direction from the relativistic effects discussed above, and thus has a tendency to cancel. The energy band studies for ReO_3 also suggest that the $10Dq$ values obtained in our work would be increased if we included the non-muffin-tin terms. For all Eu chalcogenides X_3 is the lowest conduction band, which has been found in our previous work,¹¹ and Γ_1 is the lowest conduction band at the zone center. The lowest conduction band X_3 is predominantly $5d$ -like from the Eu^{2+} ion. However, about 57% of its charge is located outside of the APW spheres. Because of the large portion of the free-electron-like charge outside of the APW spheres, both $6s$ and $5d$ electrons could play dominant roles for the interatomic interactions such as the electron transport or the ferromagnetic exchange interaction between the nearest-neighbor Eu^{2+} ions via $5d$ or $6s$ conduction bands (f - d or f - s interactions). Both the

highest $f(\uparrow)$ bands and the anion p band have fairly sizable f - p charge mixing at or near the zone center, which is due to the large overlapping of charge densities between f and p electrons as shown in Fig. 5. Their f - p mixing increases from EuO to EuSe , and the maximum f bandwidth of about 0.5 eV¹⁹ obtained in this work is attributed partly to this f - p interaction. There are two types of f - p interaction: One is the usual crystal field effect by the surrounding anion ligand field, and the other one is due to the spin-polarized exchange interaction between the $f(\uparrow)$ electrons and the induced-spin-polarized anion p electrons. In addition, there will be a strong electrostatic repulsion among f electrons, spin-orbit coupling, and the magnetic exchange interaction with the internal magnetic field below the transition temperature. The f - p interaction reduces going away from the zone center except in the X direction for EuO and EuS , and the $f(\uparrow)$ bandwidth becomes

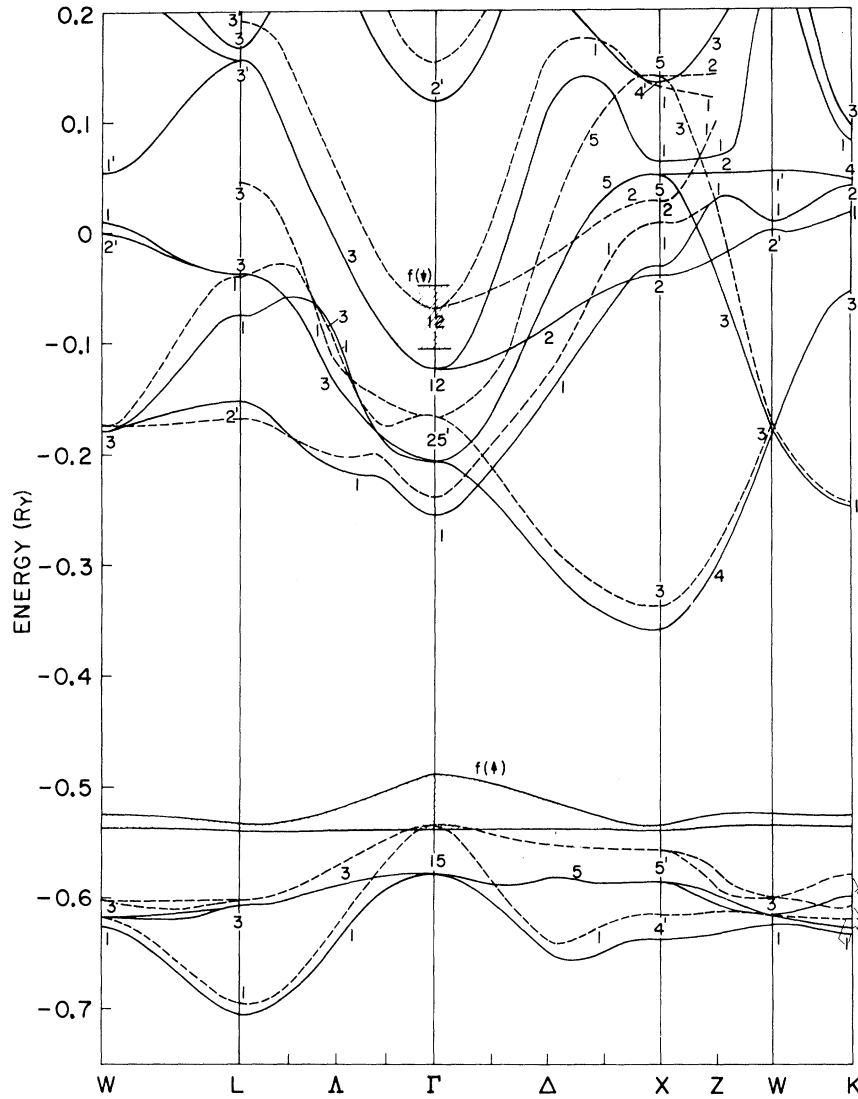


FIG. 4. Energy bands for EuSe. Solid lines for the up-spin electrons and dashed lines for the down-spin electrons.

TABLE I. Energy differences of $\Gamma_{12} - \Gamma'_{25}$ (eV).

	EuO	EuS	EuSe
Up spin	2.34	1.18	1.12
Down spin	2.65	1.38	1.33
Maximum	3.45	1.91	1.84
Average	2.50	1.28	1.22

TABLE II. APW charge analysis for up-spin bands of EuO (%).

(Eu ²⁺)	s	p	d	f	(O ²⁻)	s	p	d	Q _{out}
Γ_1 (s)	20.1	12.9	67.0
Γ'_2 (f)	96.8	3.2
Γ_{12} (d)	69.8	8.3	21.9
Γ_{15} (p)	...	1.4	...	15.0	75.6	...	8.0
Γ_{15} (f)	...	0.2	...	85.9	13.5	...	0.4
Γ_{25} (f)	99.6	0.4
Γ'_{25} (d)	56.3	4.8	39.2
X_3 (d)	41.0	4.5	54.5

TABLE III. APW charge analysis for up-spin bands of EuS (%).

(Eu ²⁺)	s	p	d	f	(Se ²⁻)	s	p	d	Q _{out}
Γ_1 (s)	13.7	19.4	66.9
Γ'_2 (f)	98.2	1.8
Γ_{12} (d)	54.8	22.2	23.0
Γ_{15} (p)	...	0.9	...	32.9	58.9	...	7.3
Γ_{15} (f)	...	0.5	...	67.9	29.4	...	2.2
Γ_{25} (f)	99.5	0.5
Γ'_{25} (d)	43.0	14.7	42.3
X_3 (d)	30.0	13.4	56.6

TABLE IV. APW charge analysis for up-spin bands of EuSe (%).

(Eu ²⁺)	s	p	d	f	(Se ²⁻)	s	p	d	Q _{out}
Γ_1 (s)	13.2	19.7	67.1
Γ'_2 (f)	98.5	1.5
Γ_{12} (d)	56.0	20.8	23.2
Γ_{15} (p)	...	0.6	...	53.0	40.8	...	5.6
Γ_{15} (f)	...	0.7	...	47.8	47.3	...	4.2
Γ_{25} (f)	99.6	0.4
Γ'_{25} (d)	43.0	14.2	42.8
X_3 (d)	29.2	13.6	57.2

narrower. This means the $f(\uparrow)$ electrons behave more or less atomiclike away from the zone center except in the X direction for EuO and EuS. The fundamental energy gaps between the $f(\uparrow)$ bands and $X_3(\uparrow)$ for the Eu chalcogenides are of the same order of magnitude as in normal semi-

conductors. The ionization energy of the first $4f$ electron is known to be the same order of magnitude as those of the loosely bound valence d electrons due to the cancellation between a strong core Coulomb attraction and the interelectronic repulsion among $4f$ electrons. Therefore we could ex-

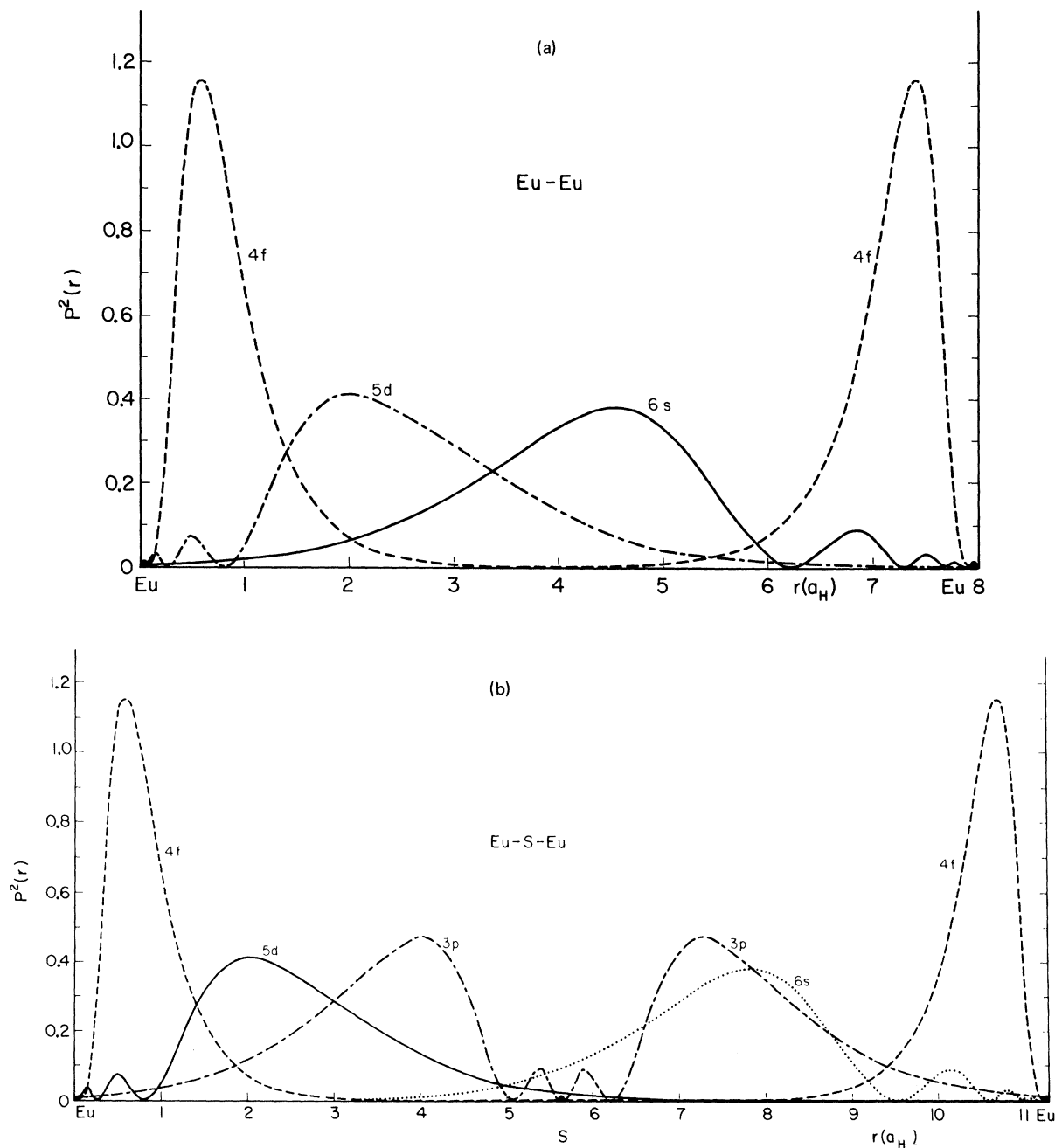


FIG. 5. Radial charge densities for EuS: (a) Eu-Eu, (b) Eu-S-Eu.

pect that one of the $4f$ electrons is somewhat loosely bound. It is also known that it requires enormous ionization energy to remove an additional $4f$ electron. Therefore we could expect almost negligible transition probability of more than one f electron from the same Eu^{2+} ion. Γ_{12} , Γ'_{25} , and the lowest conduction bands W_3 , K_1 , and Σ_3 are predominantly $5d$ -like of the Eu^{2+} ions.

The effective masses at the bottom of the conduction band X_3 have an ellipsoidal shape and the energy band at or near X_3 is expressed by

$$E(k) = E(X_3) + (\pi/a)^2 [(k_x - 2)^2 / m_x^* + (k_y^2 + k_z^2) / m_t^*], \quad (2)$$

where $m_y^* = m_z^* = m_t^*$. By fitting the energies of X_3 , $\Delta'_2(0, \frac{7}{4}, 0)$, $S_1(\frac{1}{8}, 2, \frac{1}{8})$, and $Z_4(\frac{1}{8}, 2, 0)$, we have obtained the effective masses for both up- and down-spin electrons, which are tabulated in Table V. m_x^* components are somewhat larger than the free-electron mass m_0 and increase from EuO, EuS, and EuSe. On the other hand, the m_y^* and m_z^* components are considerably smaller than m_0 and decrease from EuO, EuS to EuSe. Their average effective masses $\langle m^* \rangle$ are about 0.4~0.5 and decrease slightly from EuO to EuSe. The down-spin electrons have somewhat heavier effective masses than up-spin electrons at or near the bottom of the conduction band.

Xavier²⁰ has studied the average effective masses of EuO and EuS by using the average nature of the Bloembergen-Rowland model with experimental values of the exchange integrals J_1 and J_2 , and of the energy gaps. The results of 0.4 for EuO and 0.3 for EuS are surprisingly close to our average effective masses for up-spin electrons. However, it does not necessarily mean that the Bloembergen-Rowland-type interactions are primarily responsible for both antiferromagnetic and ferromagnetic exchange interactions in the Eu chalcogenides. Previously, we have reported that the anion p bands and the down-spin $f(\uparrow)$ bands are primarily responsible for the antiferromagnetic exchange interaction in Eu chalcogenides.²¹

It is interesting to note that the f^7 bands of Eu^{2+} ions could become $f^6(F_J)$ multiplets of Eu^{3+} ions by interband transitions from f^7 bands to the $5d$ conduction band X_3 . This process can be reversed if Eu^{3+} ions recombine with electrons to form

Eu^{2+} ions. In this case, the f^6 band of the Eu^{3+} ions behaves like hole acceptors for the anion p bands. However, these holes created at the $f(\uparrow)$ bands have such large effective masses that their mobility becomes negligibly small, and cannot contribute to the conductivity although $5d$ conduction electrons can produce n -type conduction. There is also about 30% p -like mixing for the highest $f(\uparrow)$ band, and these p -like electrons can transit to the conduction Γ_1 or to X_3 . Therefore there is another possible n -type conduction of 6s electrons. However, most of the transitions from the $f(\uparrow)$ bands should be to the d band rather than to the $6s$ band. Therefore n -type conduction is due predominantly to $5d$ electrons.

Both $6s$ - $6s$ and $5d$ - $5d$ charge density overlapings, $B(s, s)$ and $B(d, d)$ between neighbor Eu^{2+} ions decrease rapidly with increasing lattice constant. Therefore, both $6s$ and $5d$ conduction also decrease from EuO to EuTe. On the other hand, np ($n=2, 3, \dots$) charge density has one more node and is more spread out than those of $(n-1)$ p charge density. Therefore $B(p, p)$ and $B(f, p)$ between the nearest Eu^{2+} ion and the anion increase from EuO to EuTe (see Fig. 5).

In order to produce hole current at or near the energy gap the energy separation of $\Delta E_{fp} = f^7 - p$ must be smaller than that of $\Delta E_{fd} = f^7 - d$, and $B(p, p) > B(d, d)$ must be satisfied. According to our studies there will be no hole current for EuO because of $\Delta E_{fp} \gg \Delta E_{fd}$ and $B(p, p) \lesssim B(d, d)$, an almost equal amount of n - and p -type currents for EuS because of $\Delta E_{fp} \lesssim \Delta E_{fd}$ and $B(p, p) \approx B(d, d)$, and a predominantly p -type current for EuSe and EuTe because of $\Delta E_{fp} \ll \Delta E_{fd}$ and $B(p, p) > B(d, d)$. Such p -type conduction cannot be produced for energies less than the energy gap even though $\Delta E_{fp} < \Delta E_{fd}$. Such anion holes at the p bands can form excitons with electrons at the conduction bands, or produce polarons.

IV. DENSITY OF STATES

In the last few years a number of authors have studied the density of states $N(E)$, mainly for the transition and noble metals, by various experimental methods: uv photoemission spectroscopy (UPS), ion neutralization spectroscopy (INS), soft x-ray spectroscopy (SXS), and x-ray photoemission spectroscopy (XPS). Such measurements can provide useful information for understanding the electronic band structures in solids, and can be used as a tool to justify the theoretical energy band calculations. As far as transition and noble metals (Ni, Fe, Cu, and Co) are concerned there appears to be qualitative agreement between theory

TABLE V. Calculated effective masses.

	$m_x^*(\uparrow)$	$m_x^*(\downarrow)$	$m_t^*(\uparrow)$	$m_t^*(\downarrow)$	$\langle m^*(\uparrow) \rangle$	$\langle m^*(\downarrow) \rangle$
EuO	0.96	1.21	0.33	0.44	0.42	0.56
EuS	1.12	1.20	0.29	0.34	0.39	0.45
EuSe	1.15	1.20	0.27	0.31	0.36	0.41

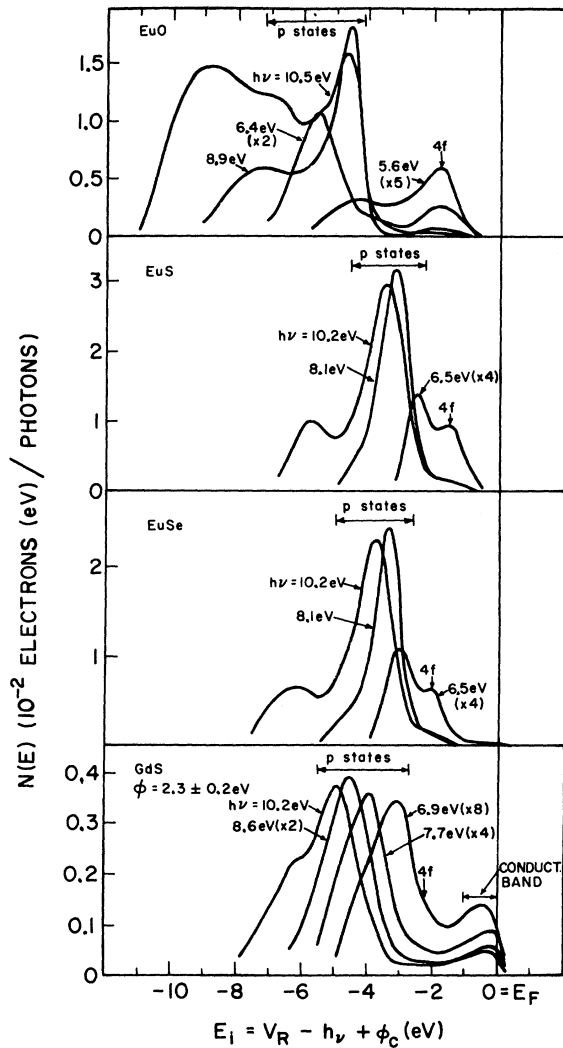


FIG. 6. Experimental density of states: (a) EuO, (b) EuS, (c) EuSe, and (d) GdS. The labels (X5), etc., indicate amplification factors (Ref. 29).

and experimental results obtained by various methods²²⁻²⁵ (except for early UPS reports²⁶). A probable exchange splitting ΔE_{ex} of the energy bands in Ni at or near E_F has been reported to be about 0.35 eV.²⁷

There are few theoretical and experimental studies on the density of states for the rare-earth metals and their alloys. Recently both Busch *et al.*²⁸ and Eastman *et al.*²⁹ have studied UPS for the Eu chalcogenides. Their results are reproduced in Fig. 6. In our work we have obtained the electronic density of states for the Eu chalcogenides for 256 points in the Brillouin zone, and the results for EuS are shown in Fig. 7. Normally, a knowledge of energy structures at more than 256

points is required in order to obtain reliable $N(E)$ curves in solids. In our case the valence bands are well isolated from each other and present work should give us fairly reliable information. On the other hand the conduction bands are quite complex and our results might not represent detailed structures which could exist. According to our results for the conduction bands, there are two peaks which are mainly derived from the t_{2g} and e_g d bands for the up-spin electrons, and three peaks for the down-spin electrons which are due to the t_{2g} and e_g d bands and the $f(\uparrow)$ bands. Both calculated and experimental data are tabulated in Table VI.

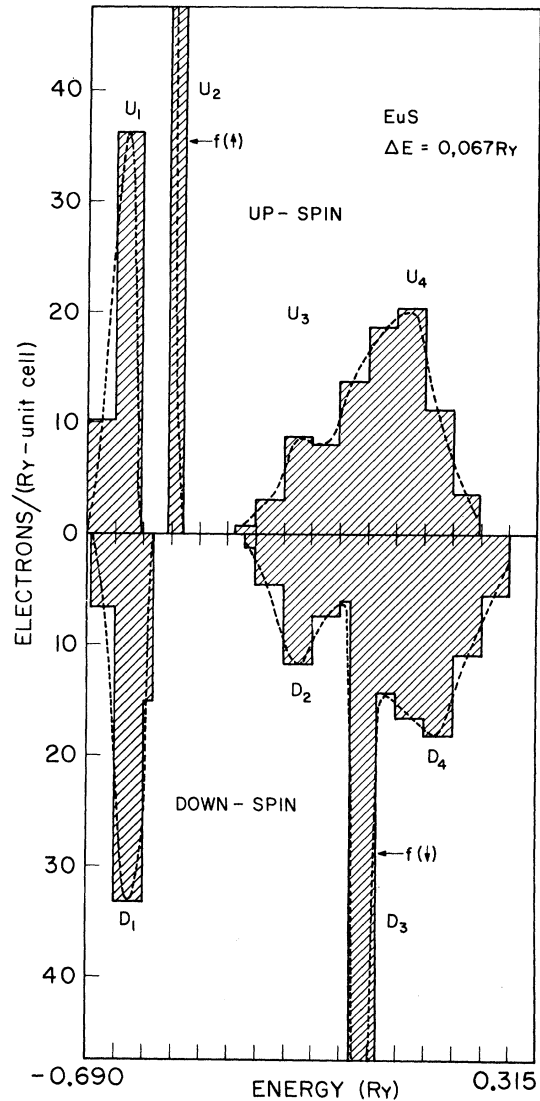


FIG. 7. Theoretical electronic density of states for EuS [number of electrons/Ry (unit cell)].

TABLE VI. Theoretical and experimental data (eV) of the valence band structures. (a) Calculated values, (b) Ref. 28, (c) Ref. 29.

		EuO	EuS	EuSe	GdS
f bandwidth	(a)	0.57	0.54	0.70	
	(b)	1.6		1.1	
	(c)	2.0	1.3	1.5	1.0
p bandwidth	(a)	2.12	2.19	2.33	
	(b)	2.0		1.3	
	(c)	3.0	2.3	2.4	2.9
f - p separation	(a)	1.41	0.44	-0.15	
	(b)	1.7		-0.4	
	(c)	2.5	0.5	-0.8	<0
Average f - p separation	(a)	2.00	1.20	0.50	
	(b)	2.5		0.8	
	(c)	3.5	2.0	1.8	1.9
Vacuum to f bands	(b)	1.7		4.6	
	(c)	1.6	4.0	4.7	4.5
p to conduction band	(a)	3.61	3.04	2.37	
	(b)	3.8		2.4	
	(c)	4.3	3.1	3.1	3.0
Vacuum to p bands	(b)	4.4		5.5	
	(c)	4.9	5.5	5.9 ^a	4.9
Work function	(b)	0.6		3.3	
	(c)	0.6	3.3	2.8	2.3

^aUsed work function of 3.3 eV (Ref. 28).

We can immediately notice from Figs. 6 and 7 that the experimentally observed density of states of f electrons $N(E, f)$ is considerably smaller than the density of states of the p electrons $N(E, p)$, that experimental f bandwidths are larger than expected for the f^7 (Eu^{2+}) bandwidth, and that the experimental p bandwidth of EuO is relatively larger than the corresponding p bandwidths for EuS and EuSe. These experimental results are in contrast to the theoretical results of a ratio of $N(E, f) : N(E, p) = 7.6$, of about 0.5 eV for the f bandwidth, and of an almost constant p bandwidth of about 2 eV for all Eu chalcogenides.

It is not clearly known why the measured $N(E, f)$ is so small. It might be related to the difficulty of releasing more than one f electron because it takes much larger ionization energies for subsequent f electrons from the same Eu atom as discussed in Sec. III. Another possibility would be a small transition probability for the transitions from the $f(\uparrow)$ bands to the vacuum level due to the small density of states at or near the vacuum level, or that transitions are nondirect.³⁰

In principle, the dominant transitions from the flat $f(\uparrow)$ bands should be direct transitions. However, the f electrons have one of the heaviest effective masses and their velocity should be very small. Accordingly the f electrons involve multi-

ple scattering with phonons and electrons before reaching the surface, or some of them are captured by existing Eu^{3+} ions which are either impurity centers or created from the Eu^{2+} ions. In this case the observed $N(E, f)$ should become considerably broader and different from the initial $N(E, f)$ which we are attempting to measure.

Another possible origin of the large f bandwidth observed could be related to the F_J (f^6) multiplets of Eu^{3+} ions (atomic F_J multiplets have a bandwidth of 0.6 eV³¹). Both Busch *et al.*²⁸ and Eastman *et al.*²⁹ have interpreted such possible F_J multiplets as arising from the Eu^{3+} ions created from Eu^{2+} ions. We expect that there are about 0.1% concentrations of Eu_2O_3 impurities in the samples. Therefore, if F_J multiplets are involved, they would be more likely from Eu^{3+} impurities rather than from Eu^{3+} ions created from Eu^{2+} ions (see Sec. V). However, we cannot rule out the possibility of F_J multiplets of Eu^{3+} being created from Eu^{2+} ions. This problem could be resolved from the similar studies with excess Eu^{3+} impurities in the sample. In any case, experiments by both Bush *et al.*²⁸ and Eastman *et al.*²⁹ do not give us proper information on the $N(E, f)$. Busch *et al.* have reported a linear variation of the f band position with incident photon energies, and Eastman *et al.* have shown f band positions independent of photon energies. According to the above UPS experiments the possible F_J multiplets of Eu^{3+} ions are located just below the $f^7(^8S_{7/2})$ bands.

The considerably larger f bandwidth of EuO comparing with the corresponding values observed for EuS and EuSe seems to indicate that the possible F_J multiplet width decreases with increasing lattice constant, or that there is a larger amount of scattering for EuO than for EuS and EuSe due to the smaller lattice constant of EuO. As we can see from Table VI, not only the experimental data of EuO disagree with theory, but two experimental results also disagree with each other. It appears that the experimental data of EuO by Busch *et al.* show better agreement with theoretical results than the results by Eastman *et al.* On the other hand, the $4p$ bandwidth of EuSe by Busch *et al.* is too small. In the case of EuS and EuSe there is reasonable agreement between theory and experiments, except for the f bandwidth. It is interesting to note that the relative positions of the top of the f and p bands among EuO, EuS, and EuSe show good agreement between theory and the experiments (Table VII).

Eastman *et al.*²⁹ have also studied UPS for GdS (see Fig. 6), in which they have found that the over-all situation is not much different from EuS, except for a partially filled valence $5d$ band, and that the possible $N(E, f)$ are further weakened and

TABLE VII. Energy differences of the highest f and p bands among Eu chalcogenides (eV): (a) Calculated values, (b) Ref. 28, (c) Ref. 29.

		p bands	f bands
EuO-EuSe	(a)	3.0	1.3
	(b)	2.9	1.1
	(c)	3.1	1.0
EuS-EuSe	(a)	0.4	0.06
	(c)	0.7	0.04

have no sign of $4f^7 \rightarrow 4f^6 5d$ transitions. These experimental results are interesting because they tell us that any reflectivity or absorption peaks from the $4f$ bands in GdS are difficult to observe. In the reflectivity or transmission experiments for Eu³ and Gd⁴ we have not observed any possible interband transitions from $4f$ bands, which could be related to almost negligible transition probability from the f (\uparrow) bands. Blodgett *et al.*,⁵ have studied photoemission measurements for Gd metal, from which they have found a large $5d$ band peak at or near E_F and a broad peak at about 6 eV below E_F . In addition there is a small peak at about 2.8 eV below E_F . They have not elaborated to discuss a small peak at 2.8 eV. The same authors²⁶ have also reported a large peak at about 5 eV below E_F for Co, Fe, and Ni, which has been found to be spurious. Referring to experimental data in Table VI for the Eu chalcogenides and GdS, it is reasonable to expect that the possible f (\uparrow) band positions in Eu and Gd metals could be located at less than 3 eV below E_F , and that a small peak at about 2.8 eV below E_F in Gd observed could be the possible f (\uparrow) band position. ΔE_{ex} for Gd should be larger than the corresponding values of 0.35 eV for Ni because the magnetic moment of Gd is more than 11 times that of Ni. The ΔE_{ex} of about 0.4 eV for Gd estimated from transmission data⁴ is a reasonable value.

Because of the exchange splitting of energy bands below T_C , the up-spin electrons have lower energy than corresponding down-spin electrons by the amount of ΔE_{ex} . Therefore, it takes more energy to lift up-spin electrons than down-spin electrons under the same experimental conditions. Accordingly, in principle, we should be able to observe such bandwidth broadening of ΔE_{ex} in the temperature-dependent studies of $N(E)$. However, practically constant $N(E)$ with variable temperatures reported for Fe and Co by XPS,²² for Ni by UPS²⁶ and INS,²⁴ and for Gd by UPS⁵ are in contradiction to above physical phenomena. A possible reason for this could be poor energy resolution of the various experimental techniques currently available.

UPS data for Eu chalcogenides, GdS, and Gd mentioned above are based on an assumption of equal transition probability from various occupied bands throughout the Brillouin zone, which is certainly not a reasonable assumption for the case of f electrons because of the small number of transitions from f band density of states observed. It would be worthwhile to carry out more experimental studies by using other techniques such as SXS, INS, or XPS to see whether we can obtain more realistic information on the $N(E, f)$.

V. OPTICAL DATA

Recently a number of authors have studied optical measurements on the Eu chalcogenides. The Busch group^{12,32} was the first to measure the fundamental absorption edges and their temperature- and magnetic-field-dependent red shifts. The high-energy optical measurements at room temperature are for polycrystalline EuSe by Zalevsky *et al.*,³³ for pressed-powder EuS by Muller and Lawson,³⁴ for single-crystal Eu chalcogenides by Guntherodt and Wachter,³⁵ for the single-crystal EuO by Grant and Suits.³⁶ More interesting optical experiments are the temperature-dependent high-energy reflectivity work for thin-film EuS by Wild *et al.*,³⁷ the temperature- and magnetic-field-dependent photoconductivity measurements for EuO, EuS, and EuSe by Bachman and Wachter,³⁸ the absorption-edge studies of EuX: SrX ($X = O, S, Se, \text{ and } Te$) by Freiser *et al.*,³⁹ high-energy magneto-optical works for single-crystal EuO, EuS, and EuSe by Feinleib *et al.*,⁴⁰ and pressure-dependent absorption-edge studies for the Eu chalcogenides by Wachter.⁴¹ There are many other interesting experimental works available for the Eu chalcogenides (see Ref. 6). Most of the early experimental data by various authors have been obtained for pressed-powder samples. It is only during the last few years that we have been able to obtain large single crystals.

Although there is abundant information on the optical effects, there have been conflicting explanations about the experimental results. Wild *et al.*,³⁷ and more recently Feinleib *et al.*⁴⁰ have found in their temperature-dependent reflectivity experiments that not only the absorption edges P_0 , but also the first reflectivity peaks P_1 in the Eu chalcogenides have shown large red shifts comparable to the absorption-edge red shifts, and that the first major peak consists of three peaks about 0.25 eV apart from each other at low temperatures (Fig. 8). On the other hand, temperature- and magnetic-field-dependent photoconductivity measurements for the Eu chalcogenides have not shown such multiple structure.³⁸

According to Feinleib *et al.*,⁴⁰ two of three

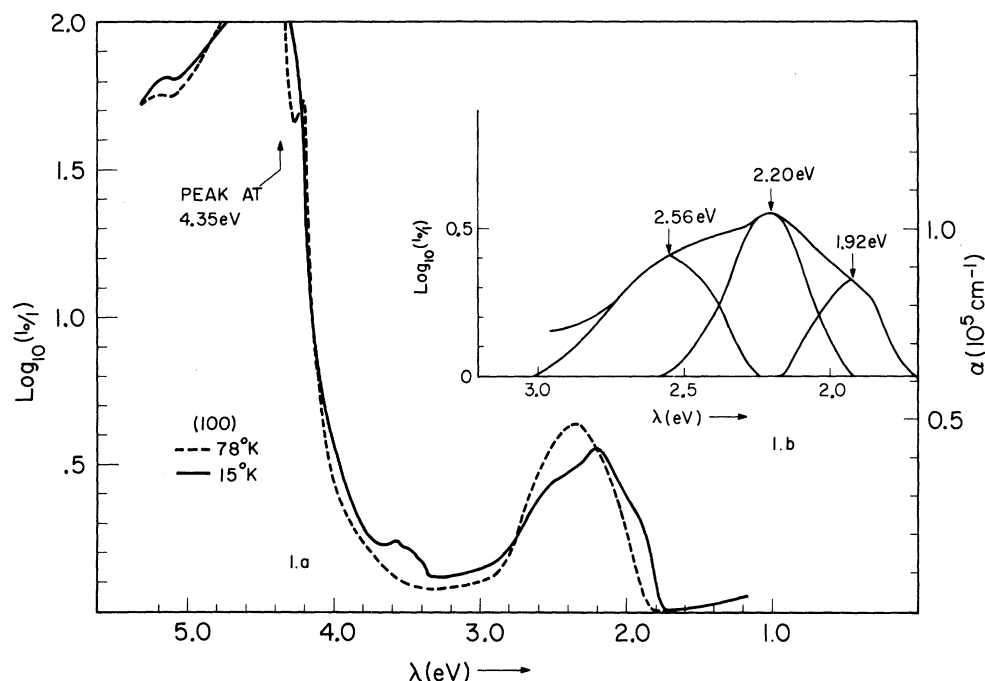


FIG. 8. Temperature-dependent reflectivity curves of EuS (Ref. 37).

peaks in the fundamental peak are polarization dependent. On the other hand, more recent experiments⁴² have shown that two of three peaks are polarization independent. Feinleib *et al.* have interpreted their experimental results of two extra peaks as multiple transitions taking place from f^6 (F_J) multiplets to the $5d$ (t_{2g}) by allowing spin-flip transitions of the f (\uparrow) electrons and by assuming an exchange splitting of 0.25 eV for the $5d$ (t_{2g}) band. Transitions from the F_J multiplets of the Eu^{3+} impurities involve single-step processes. On the other hand transitions from the F_J multiplets created from an Eu^{2+} ion involve at least two photons of a three-step process: (a) transitions of an f electron from a Eu^{2+} ($^8S_{7/2}$) ion, (b) formation of the F_J multiplets of Eu^{3+} , and (c) transitions from the F_J multiplets. Therefore the transition probability from a Eu^{3+} ion created from a Eu^{2+} ion involving a multiphoton process should be much smaller than the one from the Eu^{3+} impurities in the sample. An alternative interpretation for the two extra peaks could be the magnon-electron interaction¹⁵ which could produce the spin-flip transitions to X_3 (\uparrow). In this case we have to assume a few tenths of 1 eV for the interacting total magnon energy, which is considerably larger than the typical magnon energy of the order of 10^{-2} eV. Therefore, it is uncertain whether the magnon interaction is responsible for the extra two peaks. It might also be possible that the three peaks observed could be related to seven f (\uparrow) bands obtained in our work provided they are from

different Eu atoms. According to the model by Feinleib *et al.*⁴⁰ there must be two peaks of the density of states for the F_J multiplets which must be apart from each other by about 0.5 eV. On the other hand UPS^{28,29} have not shown any such possible structures.

Total absorption-edge red shifts observed by Busch¹² and Wachter³² are 0.25 eV for EuO, 0.18 eV for EuS, 0.17 eV for EuSe, and zero red shift for EuTe. Feinleib *et al.*⁴⁰ have attributed the above red shifts to an extra lower-energy side of the reflectivity peaks observed at low temperatures, which has been claimed for the F_J multiplets, and their estimates are 0.25 eV for both EuO and EuS, and 0.19 eV for EuSe. On the other hand, UPS measurements^{28,29} indicate that the absorption edge must be related to the f^7 bands instead of the f^6 bands. The ΔE_{ex} values of the Eu chalcogenides should be larger than the corresponding value of 0.35 eV for Ni²⁷ because the magnetic moment of the Eu chalcogenides is much larger than that of Ni. There the assumption $\Delta E_{ex} = 0.25$ eV for the Eu chalcogenides made by Feinleib *et al.*⁴⁰ is certainly an underestimate. Our estimated ΔE_{ex} values at or near the conduction $5d$ band X_3 are about 0.4~0.5 eV, which are about the same magnitude as the estimated ΔE_{ex} of Gd. In addition, the observed zero red shift of the absorption edge for EuTe could not be explained if we assume a dominant contribution of the F_J multiplets to the red shifts.

There are small red shifts of about 0.05 eV in

the paramagnetic region,¹² which are due to a lattice contraction and second-order dynamic effects. Wachter⁴¹ has reported pressure-dependent red shifts of 0.004 eV/kbar at room temperature, and 0.04 eV/kbar at low temperature. According to our lattice-constant-dependent studies for EuO, the $f(\uparrow)$ bands shift upward about 0.04 eV/kbar and the conduction band X_3 shifts downward about 0.01 eV/kbar. Therefore the absorption-edge red shifts are due mainly to the spin-polarized energy splitting of the lowest conduction band X_3 , and the f band contribution to the red shifts should be small. This type of absorption-edge red shift has been found not only for the rare-earth materials, but also for the non-rare-earth ferromagnetic semiconductors, such as CdCr_2Se_4 ($\Delta E_g \approx 0.2$ eV).⁴³ This indicates that the absorption-edge red shift is a general property for the ferromagnetic materials, and is not related to the f bands of the rare-earth substances. Several other authors⁴⁴⁻⁴⁶ have reported a similar situation. Estimated values of the absorption-edge red shifts obtained from our energy band calculations are given in Table VIII. Our results show good agreement with experimental data. In the case of antiferromagnetic materials such as EuTe, the net magnetization vanishes at all temperatures. Therefore there will be no red shift produced due to the spin-polarized energy splittings.

Room temperature optical data obtained by various authors are given in Table IX, and their probable assignments are also shown in Table X. The temperature- and magnetic-field-dependent behavior of the second peak for EuO has been observed only recently by Feinleib *et al.*⁴⁰ It is difficult to make any reliable assignments for optical peaks until more such studies have been made for other Eu chalcogenides.

The origin of the broad peaks at or near 3.0 eV is not clearly known. A possible assignment $f(\uparrow) - \Gamma_1(\uparrow)$ for P_2 is a forbidden transition ($\Delta l = 3$). However, the $f(\uparrow)$ band Γ_{15} has a considerable f - p mixing, and we should interpret this assignment as a promoted p electron of the anion to the s band Γ_1 . It is also possible that the origin of this peak might be from the F_J multiplets of the Eu^{3+} impurities in the sample as pointed out in Ref. 35.

Feinleib *et al.* have found in their reflectivity measurements that the first double P_3 and P_4 be-

TABLE VIII. Magnetic red shift (eV). Theoretical values are obtained from $\frac{1}{2}[X_3(\uparrow) - X_3(\downarrow)]$.

	EuO	EuS	EuSe
Experiments	0.256	0.18	0.17
Theory	0.25	0.17	0.16

TABLE IX. Experimental optical data (eV).

	EuO	EuS	EuSe
P_0	1.12 ^a	1.65 ^a	1.78 ^a
P_1	1.55 ^b	1.95 ^c 2.13 ^e	2.14 ^d 2.10 ^f
P_2	3.0 ^b	3.4 ^c 3.5 ^e	3.0 ^d 3.4 ^f
P_3	4.72 ^b	4.10 ^c 4.35 ^e	3.82 ^d 3.85 ^f
P_4	5.00 ^b	4.24 ^c	4.14 ^d 4.12 ^f
P_{5a}	5.75 ^b	5.65 ^c 5.40 ^e	4.76 ^f
P_{5b}		5.65 ^c	5.17 ^d 5.10 ^f
P_6	7.5 ^b	7.10 ^c	
P_7		9.40 ^c	

^aReference 13. ^cReference 34. ^eReference 37.

^bReference 36. ^dReference 33. ^fReference 32.

comes more than two peaks below the Curie temperature, which is probably due to the spin-polarized energy band splittings or spin-orbit coupling. There are at least three possible interband transitions, i. e., $t_1 = f(\uparrow) \rightarrow \Gamma'_{25}(\uparrow)$, $t_2 = f(\uparrow) \rightarrow W_3(\uparrow)$,

TABLE X. Assignments of the optical data (eV). We refer the $f(\uparrow)$ bands for the P_0 to the top of the $f(\uparrow)$ bands and the rest of them to the average values of the $f(\uparrow)$ bands.

	Assignment	EuO	EuS	EuSe
P_0	$f(\uparrow) - X_3(\uparrow)$	1.12	1.65	1.78
P_1	$f(\uparrow) - X_3(\uparrow)$	1.43	2.05	2.43
P_2	$f(\uparrow) - \Gamma_1(\uparrow)$	2.96	3.74	3.56
	$P(\uparrow) - X_3(\uparrow)$	3.55	3.18	3.09
	$P(\uparrow) - X_3(\downarrow)$	3.61	3.17	3.00
P_3	$f(\uparrow) - \Gamma'_{25}(\uparrow)$	4.68	4.30	4.24
	$f(\uparrow) - \Lambda_1^{1/4}(\uparrow)$	4.54	4.45	4.27
P_4	$f(\uparrow) - \Lambda_3^{1/4}(\uparrow)$	5.03	4.58	4.35
	$f(\uparrow) - W_3(\uparrow)$	4.32	4.57	4.71
	$P - K_1$	5.23	4.77	4.56
	$\Gamma_{15}(\uparrow) - \Gamma_1(\uparrow)$	5.27	4.73	4.40
	$\Gamma_{15}(\uparrow) - \Gamma_1(\downarrow)$	5.45	4.57	4.02
P_{5a}	$P - \Sigma_3^{3/4}$	6.36	5.44	5.10
	$f(\uparrow) - \Gamma_{12}(\uparrow)$...	5.48	4.98
P_{5b}	$\Gamma_{15} - \Gamma'_{25}$...	5.35	5.03
	$U_3 - U_1$	6.38	5.46	
P_6	$U_4 - U_2$	7.75	7.75	
	$D_3 - D_1$	8.30	7.57	
P_7	$U_4 - U_1$	10.03	9.12	
	$D_4 - D_1$	10.94	10.03	

and $t_3 = \Gamma_{15} \rightarrow \Gamma_1$. Both t_1 and t_2 should reveal red shifts, and t_3 will split into more than two peaks. At least one of these peaks should show a blue shift in the ferromagnetic region. There will be additional peaks if we include spin-orbit coupling and possible exciton structures. The transition probability from the $f(\uparrow)$ bands might be considerably smaller than from the p bands because of the small f electron density of states observed. In this case the second major peak could be dominated by transitions from p bands.

There is also more than one possible assignment for the second doublet P_{5a} and P_{5b} : from the p band to near $\Sigma_3(\frac{3}{2}, \frac{3}{2}, 0)$, and to near $f(\uparrow) \rightarrow \Gamma_{12}(\uparrow)$ and $\Gamma_{15} \rightarrow \Gamma_{25}$ (except for EuO).

The P_6 and P_7 peaks apparently involve collective transitions, and for these peaks we must rely on $N(E)$ curves. All the data taken from $N(E)$ curves are uncertain to the extent ± 0.46 eV.

BaX ($X = O, S, Se, \text{ and } Te$) has the isoelectronic configuration of the Eu chalcogenides except for f electrons. Therefore the BaX and Eu chalcogenides are expected to have similar electronic structures except for f bands. However, the $f(\uparrow)$ bands are located in between the valence p bands and the conduction d band X_3 , and both the anion p band Γ_{15} and the conduction d band X_3 are further apart from each other by about 1 eV as mentioned in Sec. II. Therefore the interband transitions from the anion p bands for the Eu chalcogenides should be larger than the corresponding ones for BaX. In fact, the first doublet for the Eu chalcogenides are about 0.2~0.6 eV larger than those for BaX. In addition the energy differences of the first doublets of the Eu chalcogenides are 0.24 eV (EuO), 0.15 eV (EuS), and 0.54 eV (EuSe), which are in good agreement with the corresponding values of 0.24 eV (BaO), 0.15 eV (BaS), and 0.54 eV (BaSe).⁴⁷ The first doublet of the BaX is probably due to the spin-orbit splitting of the anion p bands as mentioned by Zollweg.⁴⁷ Therefore, the first doublet of the Eu chalcogenides might also be from anion p bands.

VI. DISCUSSION

The f band positions are very sensitive to the exchange potential used. We have found that a reduced exchange parameter of $\frac{3}{4}$ for the magnetic Eu^{2+} ions produced proper energy gaps and the relative f band positions for the Eu chalcogenides. Our APW calculations indicate that the $f(\uparrow)$ bands are the highest valence bands, and that the lowest conduction band is the $5d$ band X_3 . The calculated maximum $f(\uparrow)$ bandwidth is about 0.5 eV which disagrees with UPS data of about 1.5 eV.^{28,29} The up- and down-spin f band separation is about 6 eV.

We have obtained an almost constant anion p bandwidth for the Eu chalcogenides, which is in contrast to a much larger p bandwidth for EuO than for the rest of the Eu chalcogenides obtained by UPS. The $N(E, f)$ obtained by UPS is too small which could be due to multiple scattering with phonons and electrons, and to recombination with Eu^{3+} centers (which could also cause the large f bandwidth observed).

Previously predominant contributions to the absorption red shifts and the multiple structures of the fundamental reflectivity peaks have been attributed to the F_J multiplets of the Eu^{3+} ions created from Eu^{2+} ions which involves multiple photon process under the assumption of spin-flip transitions from f bands and an exchange splitting of 0.25 eV for the $5d$ conduction band.⁴⁰ In our present report the magnetic red shifts observed have been attributed to the exchange splitting of the X_3 band below T_C which is estimated to be about 0.4~0.5 eV for the ferromagnetic Eu chalcogenides, and becomes zero for the antiferromagnetic EuTe. On the other hand, the multiple structure of the fundamental peak could also be due to the magnon-electron interaction or to the seven $f(\uparrow)$ bands obtained in our work provided they are from different Eu^{2+} ions.

Probable origins of the high-energy reflectivity peaks have been assigned. However, further studies of the temperature- and magnetic-field-dependent optical effects are necessary to justify them.

We expect that there will be predominantly n -type conduction for EuO, an almost equal amount of n - and p -type conduction for EuS, and a predominantly p -type conduction for EuSe and EuTe.

The conductivity due to the $5d$ electrons decreases rapidly from EuO to EuSe. Therefore the probability of recombination of the occupied $5d$ electrons with the p holes or with Eu^{3+} should increase from EuO to EuSe. The recombination energy emitted must be smaller than the excitation energy. This is because of the exchange splitting of the $5d$ bands. Another reason for this is due to the internal magnetic field disturbance and to the local charge redistribution (the occupied bands are lowered and the hold bands shift upwards). In the case of EuSe both $f(\uparrow)$ and p electrons can be excited to the $5d$ bands by small increments of the excitation energy (~0.5 eV) from the absorption edge because of the f - p overlapping. In this case both $5d$ - p hole and $5d$ - Eu^{3+} recombinations could take place. It is also possible that the p hole bands could be located above the $f(\uparrow)$ bands, depending on the magnetic structure of EuSe, and can contribute further reduction of the recombination energy emitted because of the exchange splitting of the p bands.

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