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# Optical Properties of the Europium Chalcogenides*

**Abstract:** The measured optical properties of the Eu chalcogenides are surveyed in an attempt to determine those aspects of the electronic structure of these materials that have been established. Optical absorption as well as optical and magneto-optical reflectivity data are discussed, along with the results of photoconductivity, photoluminescence and photoemission measurements and of magneto-optical measurements in the vicinity of the absorption edge. It is concluded that the fundamental absorption edge is due to the onset of $Eu^{++}$ 4f to 5d transitions of the type $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(T_{2g})$ and that a higher energy reflectivity peak is primarily due to $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(E_g)$ transitions, although anion p-valence band to Eu conduction band transitions may also be involved. The principal unanswered questions involve the relative positions of the Eu 6s and $5d(T_{2g})$ states, the breadth of the 5d levels and the role played by exciton effects in the 4f to 5d optical transitions.

## Introduction

The optical properties of the magnetic semiconductors EuO, EuS, EuSe and EuTe have been studied by a number of workers using many different experimental techniques. Optical and magneto-optical studies have revealed structure associated not only with the absorption edge but also at considerably higher photon energies. Perhaps the most striking optical phenomena observed in the Eu chalcogenides are the large magneto-optical effects associated with the absorption edge. In this region these crystals show strong linear and circular dichroism and birefringence in the magnetic state leading to large Kerr effects and Faraday rotation. In addition, these crystals show a large shift of the absorption edge to lower energies as the temperature is reduced through the ordering temperature or as a magnetic field is applied. In this survey we will review some of these results as well as some related studies on photoconductivity, photoemission and photoluminescence. It will be seen that considerable information regarding the electronic structure of these materials has been obtained through studies of their optical properties, but a number of rather important questions remain unanswered.

The magnetic and optical properties of the Eu chalcogenides have been recently reviewed by several workers from different points of view emphasizing different aspects of the field.[1-5] Some of the pertinent magnetic and optical data are given in Table 1. EuO and EuS are both ferromagnetic whereas EuSe orders antiferromagnetically but becomes ferromagnetic with the application of a small external magnetic field. EuTe appears to be a typical antiferromagnet. The respective optical energy gaps at 300°K are also given in the table. These, however, are a strong function of temperature, as will be discussed below.

## Optical properties of $Eu^{++}$ ions in crystals

Considerable information regarding the optical properties of the europium chalcogenides has been obtained by studying the properties of $Eu^{++}$ ions in various host crystals.[1] The optical spectra of $Eu^{++}$ in $CaF_2$, $SrF_2$ and $BaF_2$ exhibit two broad absorption bands which have been identified with transitions from the $4f^7(^8S_{7/2})$ ground state of $Eu^{++}$ to states of the $4f^65d$ configuration.[6] The two bands arise due to the tetrahedral crystal field splitting of the 5d states into lower energy $E_g$ and higher energy $T_{2g}$ levels. The lower energy transitions show considerable structure which has been identified with the multiplet splitting of the final $4f^6$ configuration. This structure is not observed in the higher energy $T_{2g}$ transitions, presumably because it is washed out by the 5d spin-orbit splitting in the $T_{2g}$ states which is absent in the $E_g$ states. Very similar structure is observed in the optical absorption spectra of $EuF_2$. This is shown in Fig. 1 along with the absorption spectra of EuO and EuSe for comparison. If the final $4f^6$ configuration is analyzed in the L-S coupling scheme the lowest energy multiplet is $^7F_J$ with 7 levels ($J = 0, 1, \cdots 6$). The approximate expected spacing[8] of these levels is shown in the figure. The clear appearance of this multiplet structure is a strong indication that the final $4f^65d$ configuration can be analyzed in the fashion $4f^6(^7F_J)5d(E_g)$ and $4f^6(^7F_J)5d(T_{2g})$ and that the coulomb interaction between the 4f and 5d electrons is small.

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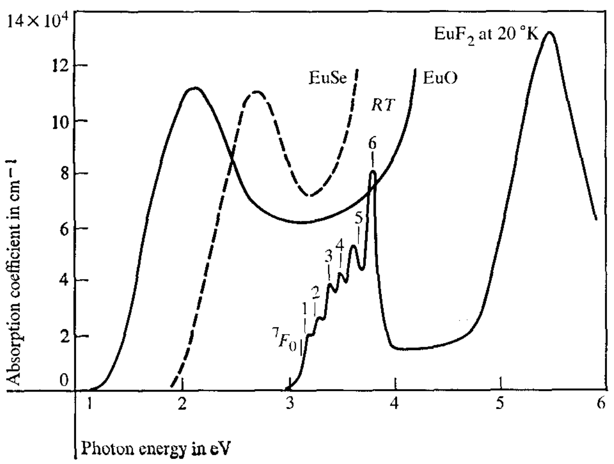


**Figure 1** Absorption spectra for evaporated films of EuSe, EuO and $EuF_2$ (after Freiser, Methfessel and Holtzberg, Ref. 7).

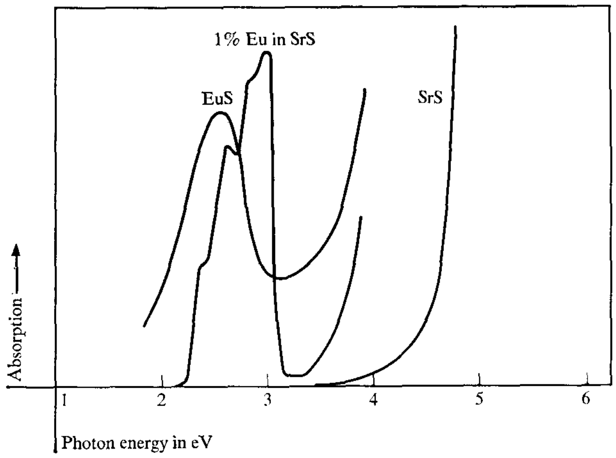


**Figure 2** Absorption spectra for evaporated films of EuS and for $Eu^{++}$ ions in SrS (after Freiser et al., Ref. 9), compared to the absorption edge of undoped SrS (after Zollweg, Ref. 10).

In the Eu chalcogenides the crystal field has octahedral symmetry such that the positions of the $T_{2g}$ and $E_g$ levels are reversed, with the $T_{2g}$ levels lying lower. A closer comparison might thus be expected between the absorption spectra of the Eu chalcogenides and that of $Eu^{++}$ in the alkaline earth chalcogenides which have the same rock salt structure. In Fig. 2 the optical absorption of EuS and that of 1% $Eu^{++}$ in SrS is shown. Included also is the absorption edge of pure SrS for comparison. Europium is electronically equivalent to Sr except for the addition of seven 4f electrons. We can thus identify the additional low energy absorption which is associated with the absorption edge in EuS, and in the other Eu chalcogenides, with the onset of 4f to 5d transitions on $Eu^{++}$. From the above arguments these are most likely of the form $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(T_{2g})$.

The room temperature reflectivity spectra of EuO, EuS, EuSe and EuTe are shown in Fig. 3. In addition to the lower energy peak, $E_1$, which we identify with the $T_{2g}$ transitions, a higher energy peak, $E_2$, is observed which we tentatively identify with $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(E_g)$ transitions separated from the $E_1$ peak by the crystal field splitting of the 5d states. The energies of the optical transitions observed in the Sr and Eu chalcogenides are given in Table 2. Note the close comparison between the lattice constants of the Sr and Eu compounds, giving further indication that the band structures of the two series should be similar except for the 4f electrons. It would appear that the transitions giving rise to the $E_2$ peak in EuO, EuS and EuSe are energetically different from those determining the absorption edge in the Sr compounds, such that the $E_2$ peak also may arise at least in part from 4f to 5d transitions. However, the $E_2$ energy in EuTe and that of $I_a$ in SrTe are quite similar and may identify the same transitions, which could be anion p-valence band to either 5d or 6s cation conduction band. The absorption

**Table 1.** Magnetic and optical data of Eu chalcogenides.[a]

| | *Curie temperature*, °K | *Magnetic order* | *Ordering temperature*, °K | *Absorption edge at* 300°K, eV |
|---|---|---|---|---|
| EuO | 76 | Ferro- | 69.4 | 1.12 |
| EuS | 19 | Ferro- | 16.5 | 1.64 |
| EuSe | 9 | Antiferro-<br>Ferro- | 4.6<br>2.8 | 1.85 |
| EuTe | −6 | Antiferro- | 7.8 to 11 | 2.0 |

[a] After Methfessel and Mattis, Ref. 1.

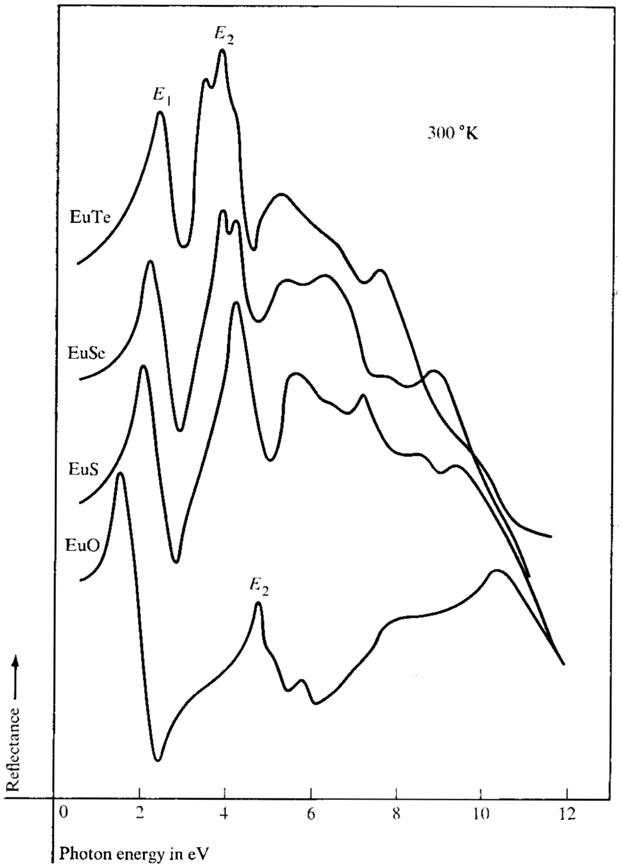


**Figure 3** Room temperature reflectivity spectra of EuO, EuS, EuSe and EuTe single crystals (after Scouler et al., Ref. 11).

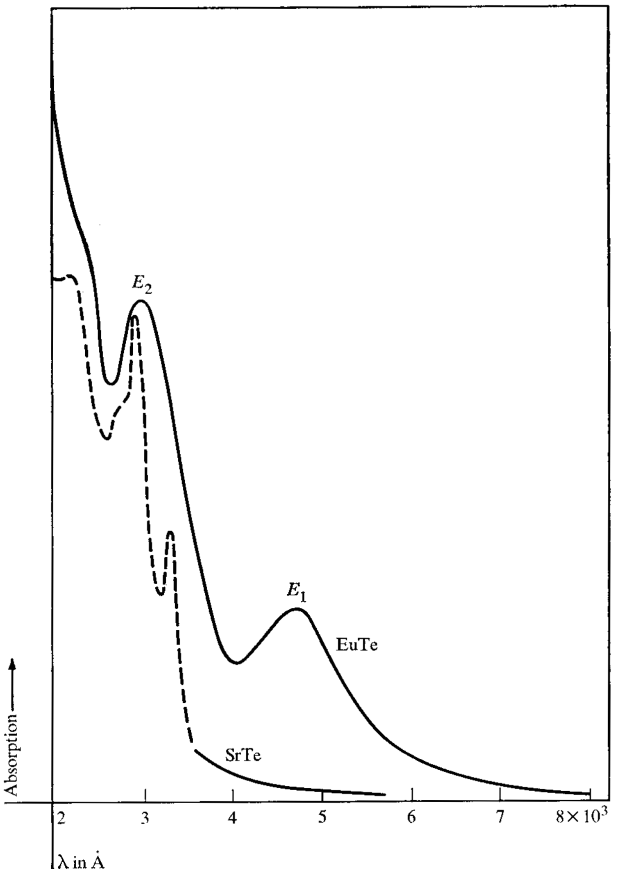


**Figure 4** Optical absorption spectra of thin films of EuTe and SrTe at room temperature. The dashed line is taken from Zollweg (Ref. 10) for −60°C (after Holtzsberg, McGuire and Methfessel, Ref. 12).

spectra of EuTe and of SrTe are shown in Fig. 4. Note the corresponding structure in the two materials in the vicinity of the $E_2$ energy. Consequently, although the $E_2$ peak is probably mostly composed of Eu $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(E_g)$ transitions these are possibly mixed, especially in the case of EuTe, with anion p-valence band to cation conduction band transitions.

An energy level diagram that describes these results is shown in Fig. 5. The optical energy gap, $\epsilon_g$, is given by the absorption edge from Table 1 and the crystal field splitting, 10 $Dq$, by the energy difference between $E_1$ and $E_2$ from Table 2. From the above discussion we expect the energy gap between the anion p bands and either the 6s or $5d(T_{2g})$ states to be given approximately by the energies $I_a$ of the corresponding strontium compounds. We will note below, however, that this is not in agreement with the interpretation of recent photoemission data. The principal questions that remain to be answered are whether the 6s states lie above or below the $5d(T_{2g})$ levels and just how broad the $5d(T_{2g})$ and $5d(E_g)$ levels are.

Although the structure of the optical absorption and reflectivity data indicates that the 5d states form relatively narrow $T_{2g}$ and $E_g$ levels as indicated in Fig. 5, recent energy band calculations[14] yield a 5d band some 10 eV wide composed of overlapping $T_{2g}$ and $E_g$ states. Exciton effects arising from the coulomb attraction between the excited 5d electron and the $Eu^{+++}$ $4f^6$ configuration could,

**Table 2.** Optical transitions in Sr and Eu chalcogenides.

| | $a$, Å | $I_a$,[a] eV | | $a$, Å | $E_1$,[b] eV | $E_2$,[b] eV |
|---|---|---|---|---|---|---|
| SrO | 5.10 | 5.71 | EuO | 5.14 | 1.55 | 4.72 |
| SrS | 5.87 | 4.76 | EuS | 5.96 | 1.95 | 4.16,4.27 |
| SrSe | 6.23 | 4.42 | EuSe | 6.19 | 2.20 | 3.88,4.17 |
| SrTe | 6.48 | 3.73 | EuTe | 6.60 | 2.37 | 3.43,3.83 |

[a] From absorption data on thin films at −160°C after Zollweg, Ref. 10.
[b] From reflectivity data on single crystals at room temperature after Scouler et al., Ref. 11.

however, cause a strong enhancement of the optical structure associated with the onset of transitions to the 5d band, giving the illusion of narrow bands. The role of exciton effects in the optical transitions of the Eu chalcogenides has been discussed at some length by Kasuya and Yanase.[15] However, the importance of these effects in the 4f to 5d transitions remains as one of the more interesting unanswered questions regarding the electronic structure of these materials.

## Optical properties associated with the band edge

A wealth of optical and magneto-optical phenomena are associated with the onset of $4f^7 \rightarrow 4f^6 5d$ transitions which are responsible for the absorption edge in the Eu chalcogenides. These have been studied by many workers and provide much of the interest in these materials. A partial list of the effects that have been studied to date is collected in Table 3. In this Section we discuss briefly the red shift and the optical dichroism and birefringence, leaving the discussion of reflectivity for the next section and that of the combined effects of photoconductivity, photoluminescence and photoemission for the last Section. The optical absorption spectra of EuO and EuSe at room temperature are shown in Fig. 1 and of EuS and EuTe in Figs. 2 and 4, respectively. The general features are quite similar for all materials, although structure changes and relatively large shifts with temperature and magnetic field occur. The shift of the absorption edge with temperature in EuO, EuS and EuSe for magnetic fields $H = 0$ and $H = 19$ kG is shown in Fig. 6. Also shown are the respective ordering temperatures for these materials. Rys, Helman and Baltensperger[43] have calculated the absorption edge shift based on a band model for the excited electron. In their model a sizeable red shift occurs at temperatures above the Curie temperature $T_c$ in zero magnetic field due to effects of near-neighbor spin correlations. Below $T_c$ the conduction band splits and additional shifting occurs as the material orders ferromagnetically. In contrast to this band model, Yanase and Kasuya[15] have interpreted the red shift in terms of a "magnetic exciton" model in which the excited 5d electron is localized near the $Eu^{+++}$ core. In this model the red shift is entirely determined by the temperature dependence of the nearest-neighbor spin correlation functions.

**Table 3.** Studies of the optical properties of the Eu chalcogenides.

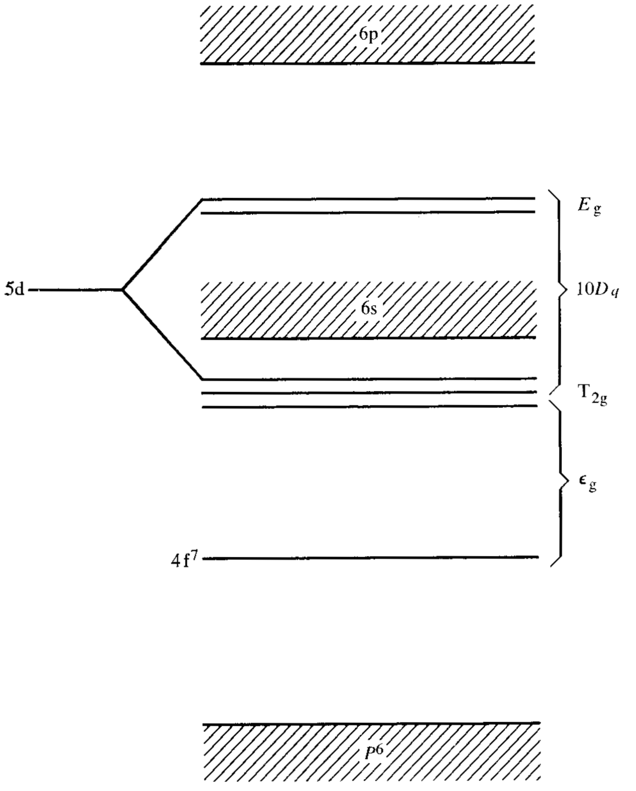
| | *Absorption spectra* | *Red shift* | *Optical dichroism* | *Optical birefringence* | *Kerr effect* | *Reflectivity* | *Photo-conductivity* | *Photo-luminescence* | *Photo-emission* |
|---|---|---|---|---|---|---|---|---|---|
| EuO | Optical at 300°K (7, 9, 13,16);[a] at 8°K (17); I. R. at 20°K (18); vs $T$ in Gd doped (19); vs Eu content (47) | vs $T$ (9, 22); at $H = 0$ and 19 kG (2) | Absorption edge shift at 77°K (9) | Faraday rot. at 5°K (17); at 10°K and 63°K in Gd doped (19); I. R. at 20°K (18); vs Eu content (47) | Spectra at 12°K (25); on mirrors (26); at 6°K in Gd doped (19); with oxide films (27) | Spectra at 300°K (28, 20); polarized spectra vs $H$ and $T$ (29) | Sensitivity vs $H$ and $T$ (34, 35) | | Spectra at 300°K (40, 41) |
| EuS | Optical at 300°K (9, 13, 16, 20); at 78° K and 15°K (21); magneto-optical at 60°K and 5°K (20) | vs $T$ (9, 22); at $H = 0$ and 19 kG (2) | | Faraday rot. spectra at 6°K (20) | Spectra at 8°K (25) | Spectra at 300°K (30, 20); polarized spectra vs $H$ and $T$ (31) | Spectra at 300°K (36); spectra vs $T$ (34); sensitivity vs $H$ and $T$ (34, 35) | | Spectra at 300°K (40); polarization vs $H$ at 4°K (42) |
| EuSe | Optical at 300°K (7, 9, 13, 16, 20); magneto-optical at 20°K and 5°K (20) | vs $T$ (22); at $H = 0$ and 19 kG (2) | vs $H$ at 4°K and spectra at 300°K, 77°K and 4°K (23) | Faraday rot at 300°K (16); linear and circular vs $H$ at 4°K (24) | | Spectra at 300°K (32, 20); polarized spectra vs $H$ and $T$ (31) | Spectra at 300°K (36); sensitivity vs $H$ and $T$ (37) | Intensity and spectra vs $H$ and $T$ (38); excitation and luminescence spectra vs $H$ and $T$ (39) | Spectra at 300°K (40, 41); polarization vs $H$ at 4°K (42) |
| EuTe | Optical at 300°K (12, 13) | vs $T$ (22) | | | | Polarized spectra vs $H$ (33) | | | |

[a] The numbers in parentheses are References.

The amount of shift depends on the amount that the 5d wave function extends over neighboring Eu ions. If the localization were negligible the 5d state would experience the full 4f-5d exchange interaction, whereas if the excitation were fully localized on the central ion, no exchange splitting or red shift would be expected. The situation in EuO, EuS and EuSe appears to be intermediate between these extremes. The red shift in EuO has been shown by Freiser et al.[9] to follow very closely the experimentally determined nearest-neighbor spin-spin correlation function as expected from the "magnetic exciton" model.

As mentioned above, some of the most exciting and potentially important properties of the europium chalcogenides are their unusually large magneto-optical effects. As an example of optical dichroism, the absorption of EuSe measured[23] using polarized radiation at 4.2°K in a magnetic field of 15 kG shows a shift of almost 0.1 eV between the edges for right and left circularly polarized light. Large birefringence effects associated with this are also observed. For example, the Faraday rotation at 5°K and 20.8 kG in EuO[17] reaches a maximum of $4.9 \times 10^5$ deg/cm at 0.66 $\mu$m. At 6°K and 6.75 kG the maximum in EuS[20] is $5.5 \times 10^5$ deg/cm at 0.56 $\mu$m. EuO also has a large Faraday rotation in the infrared, where it is quite transparent.[18] The absorption coefficient at 20°K is less than 0.5 $\text{cm}^{-1}$ in the range between 2.5 and 9$\mu$m and less than 1.0 $\text{cm}^{-1}$ at 10.6 $\mu$m. At 20°K and 9 kG the Faraday rotation varies from 660 deg/cm at 10.6 $\mu$m to $3 \times 10^4$ deg/cm at 2.5 $\mu$m and about $2 \times 10^5$ deg/cm at 1.5 $\mu$m. Also associated with these phenomena are large Kerr effects which have been observed under a variety of conditions.[25-27] Further references to this and to other results on magneto-optical phenomena are given in Table 3.

**Figure 5** Qualitative energy level scheme for the Eu chalcogenides (after Methfessel, Holtzberg and McGuire, Ref. 13).



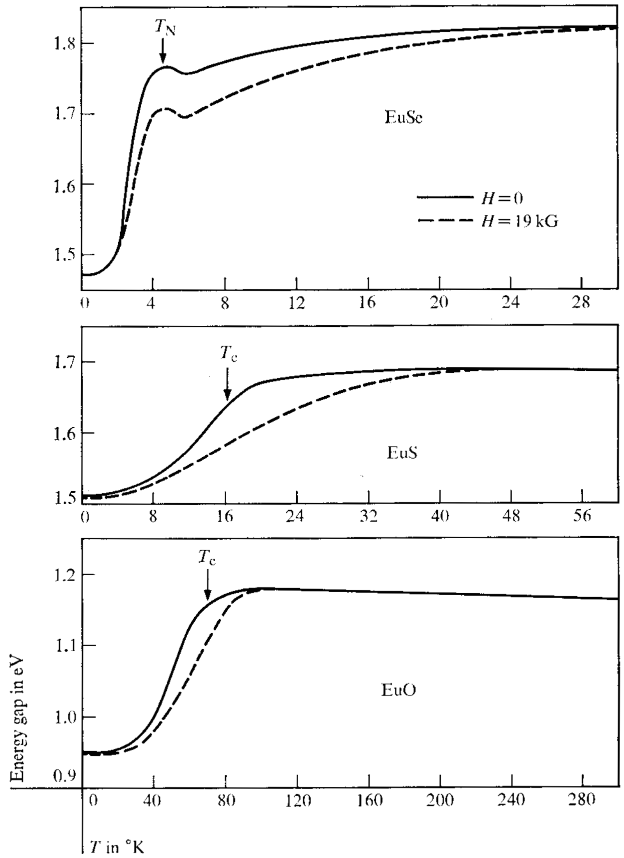


**Figure 6** Shift of the absorption edge of EuO, EuS and EuSe with temperature for $H = 0$ and $H = 19$ kG (after Busch and Wachter, Ref. 2).

## Reflectivity

The effects of magnetic ordering on the $E_1$ and $E_2$ reflectivity peaks of EuO, EuS, EuSe and EuTe shown in Fig. 3 have been studied as a function of temperature and magnetic field using both polarized and unpolarized radiation.[11,29,31,33] In EuO, EuS and EuSe the behavior is qualitatively the same. The $E_1$ peak shifts slightly with decreasing temperature and, at temperatures considerably above $T_c$, is resolved into a polarization-dependent doublet in an external magnetic field. At lower temperatures, below $T_c$, this doublet becomes split into a triplet. The results for EuSe are shown in Fig. 7. The results observed in EuO and EuS are quite similar. The $E_2$ peak is also

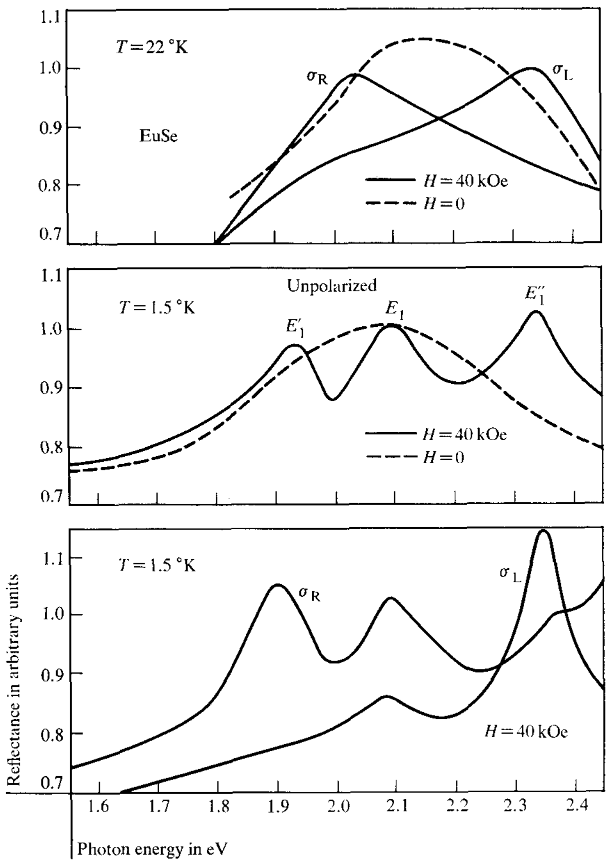


**Figure 7** Polarized and unpolarized reflectivity of EuSe for $H = 0$ and 40 kG at 1.5°K and 22°K (after Pidgeon et al., Ref. 31).

resolved into a doublet above $T_c$. However, in contrast to the $E_1$ peak, this same structure is observed both above and below $T_c$. Very similar effects have recently been observed in the absorption spectra of thin films of EuS and EuSe by Guntherodt, Schoenes and Wachter.[20] This polarization-dependent reflectance structure has been recently analyzed by Hanus, Dimmock and Feinleib[44] in terms of the transition probabilities from the $4f^7(^8S_{7/2})$ ground state to each of the several $4f^6(^7F_J)5d(T_{2g})$ and $4f^6(^7F_J)5d(E_g)$ levels. This has also been recently discussed by Guntherodt, Schoenes and Wachter.[20] In the calculation, a preferential population of the spin-down states of the $4f^7(^8S_{7/2})$ ground state was assumed to correspond to a partially magnetized situation. The oscillator strengths for transitions from the lowest sublevel, $M_J = -7/2$, to each of the $4f^6(^7F_J)$ multiplet levels and 5d states were calculated, and it was found that transitions to the lower $J$ states are favored for right circularly polarized radiation, whereas transitions to the upper $J$ states are favored for left circularly polarized radiation. The high-temperature resolution into right and left circularly polarized components thus depends only on the preferential population of the spin-down components of the initial state, which is proportional to the magnetization. The energy resolution is in reasonably good agreement with the expected separation of the $^7F_J$ multiplet levels of the final state and does not require any exchange splitting of the 5d states. The additional splitting of the $E_1$ peak into a triplet below the ordering temperatures can thus be ascribed to the exchange splitting of the 5d states that occurs in the ordered phase. The $E_2$ peak is not observed to split further since half of the transitions are electric-dipole-forbidden.

In this model we have two separate phenomena. At high temperatures in an external magnetic field the crystal is magnetized, resulting in a polarization of the $^8S_{7/2}$ configuration, but the 5d states are not split. Support for this is obtained from measurements of the magnetization and red shift in EuSe at temperatures above the ordering temperature. For example, at 22°K in an external field of 40 kG the magnetization is approximately 40 percent of the saturated value,[45] whereas the band edge shift is less than 5 percent of the total shift observed[2] at $T = 0$. (See Fig. 6) The 5d states split only at lower temperatures below $T_c$ as the material orders magnetically. This implies at least a partial localization of the excited state since, on a band model, the splitting should be roughly proportional to the magnetization. This is at least qualitatively consistent with the "magnetic exciton" model of Kasuya and Yanase.[15] The persistence of the polarization structure in the $E_2$ peak at temperatures well above the ordering temperature indicates that this peak also involves, at least partly, transitions from the $4f^7$ ground state.

Magnetic ordering effects on the polarized optical reflectivity of EuTe at 1.5°K in magnetic fields up to 97.4 kG have also been studied.[33] EuTe is an ordinary antiferromagnet at low temperatures in low and intermediate magnetic fields. Under these circumstances the alternating spin structure reduces the lattice periodicity and introduces new superzone boundaries into the Brillouin zone. On these superzone boundaries each 5d band is split into two components, a lower energy one in which the d electron spin functions alternate so as to be aligned with the 4f electrons on each site, and a higher energy one in which the spin wave functions are oppositely aligned. The splitting occurs only over the superzone boundary and the effects of exchange diminish as one moves away from these boundaries in $k$-space. Each band remains doubly degenerate by time reversal, such that the reflectance is expected to be unpolarized, as is observed experimentally. At low and intermediate magnetic fields the $E_1$ reflectivity peak is observed to be a polarization-independent triplet. The structure may be due to transitions to the 5d band at different points in the Brillouin zone and may be associated with the superzone boundaries. In an increasing magnetic field the 4f spin states tend toward ferromagnetic order, causing the 5d bands to become spin-split throughout the Brillouin zone and reducing the discontinuity at the superzone boundary. In the fully ferromagnetic state, $H > 75$ kG,[46,33] the superzone boundaries are effectively removed. Experimentally, as the field is increased the higher energy $E_1$ reflectance peak disappears and new low energy structure is introduced. This may be due to the removal of the critical density of states associated with the superzone boundary and the introduction of the splitting associated with the ferromagnetic order. A polarization-dependent $E_1$ triplet is observed in EuTe at high fields, which is qualitatively identical to that observed in ferromagnetic EuO, EuS and EuSe at low and intermediate fields. The magnetic field dependence of the $E_2$ structure is rather more complicated and is not easily interpreted. Recall, however, that especially in EuTe this peak may be due to a combination of 4f to 5d and valence to conduction band transitions.

### Combined effects

As indicated in Table 3, photoconductivity, photoluminescence and photoemission have also been studied in the europium chalcogenides. The photoconductivity spectra of EuO and EuS have been measured as a function of temperature and magnetic field,[34,35] and it was found that the sensitivity spectra essentially follow the shifts of the absorption edge and could be associated with it. This would appear to be in contradiction of the model in which the absorption edge arises due to transitions to a bound exciton state, since this would not contribute to the conductivity. However, the exciton could break up into a free hole and electron or, if the 6s band lies below the $5d(T_{2g})$ levels as has been proposed by Yanase and Kasuya,[15] the $4f^6 5d$ exciton could decay into a free 6s electron and a localized 4f (hole), giving rise to the photoconductivity.

Photoluminescence has been observed in EuSe at energies somewhat below the absorption edge.[38] At 5.2°K and $H = 0$ the emission peak is at 1.45 eV, whereas the absorption edge from Fig. 6 is approximately 1.76 eV. Furthermore, in a magnetic field of 19 kG the emission peak shifts 0.11 eV to 1.34 eV, whereas the absorption edge shifts only about 0.06 eV to 1.70 eV. This difference has been ascribed[15] to a difference in the radial extent of the magnetic exciton in the absorption and emission processes. Namely, after the absorption occurs, the lattice relaxes around the magnetic exciton, allowing the wave function to spread out such that it extends over more Eu neighbors during the recombination process. As a result, the magnetic ordering has a greater effect on the energy of the luminescence peak than on the absorption edge.

Recently, room temperature photoemission measurements on the Eu chalcogenides have been reported by Busch, Cotti and Munz[41] and by Eastman, Holtzberg and Methfessel.[40] The latter authors have observed structure which they have interpreted as due to 4f to conduction band and p-valence to conduction band transitions. Using the observed optical energy gaps to determine the 4f to conduction band energies, they have obtained valence to conduction band energy gaps of 4.3, 3.1 and 3.1 eV for EuO, EuS and EuSe respectively. These energies are, however, considerably less than the energy gaps observed in the corresponding Sr compounds indicated in Table 2 and are also less than those observed in the corresponding Ba compounds.[10] The reason for this difference is not understood.

Finally, polarized photoemission measurements have been made on films of EuS and EuSe near liquid helium temperature in magnetic fields up to 33 kG perpendicular to the film.[42] The photoemitted electrons show a markedly high degree of spin polarization reaching a value of 34 percent in EuS at a photon energy of 5.0 eV. It has been argued[42] that this high value further indicates that the initial state of the optical transition is the fully polarized $4f^7(^8S_{7/2})$ level. In addition, this provides another potentially important application for these materials.

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