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Low-temperature optical absorption and magnetic circular dichroism of YbTe thin films

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We have measured the optical absorption and the magnetic circular dichroism (MCD) of a YbTe thin film in the visible and ultraviolet at 300 and 10 °K. The general features of the spectra can be understood in terms of $4f^{14}$ (Yb^{2+}) $\rightarrow 4f^{13}\,5d$ (t_{2g}, e_g) transitions by neglecting the coupling between a d electron and the $4f^{13}$ core, as in the case of europium chalcogenides. The MCD enables us to identify the diamagnetism of YbTe and to estimate the spectroscopic splitting factor of the lowest excited state. The observation that the first absorption band due to $f \rightarrow d$ transition is around 2 eV supports the results of recent pressure-volume studies of YbTe.

INTRODUCTION

Rare-earth monochalcogenides have attracted much attention in recent years because of their interesting magnetic and electric properties. However, it is from a study of their optical properties in the form of thin films that much information regarding their electronic structure has been gained.[1–3] In 1963, McClure[4] foresaw the possibility of the 4*f* levels of Yb being located above the valence band in the case of YbS. For the Eu chalcogenides, Methfessel[5] first proposed a band structure in which the 4*f* levels of Eu are localized between the valence and conduction bands formed, respectively, by the *p* orbitals of the chalcogen and 5*d*-6*s* orbitals of Eu and this was able to explain qualitatively the optical spectra.[1] We have reported earlier on the room-temperature optical absorption of YbTe and YbSe films and used the above arguments to explain the spectra.[2] We further report here on the optical spectra and on the magnetic circular dichroism (MCD) of YbTe at 300 and 10 °K and apply the results of a recent calculation[6] based on a localized model to explain the general features of the spectra.

SAMPLE CHARACTERIZATION

Several samples of YbTe films were obtained by co-evaporation of the respective elements in vacuum onto heated substrates of Pyrex, mica, and CaF_2.[2,7] We have retained a 1000-Å-thick film deposited on CaF_2 for the present study. X-ray analysis shows a NaCl structure with a lattice constant of 6.360 ± 0.003 Å in close agreement with that measured on a single crystal[8]; the film had a (222) growth axis. From the x-ray diffraction profiles, the grain size is estimated to be around 750 Å. This film looked pale blue by transmission. It has been reported that YbTe single crystals decompose into a powdery mass when exposed to air for a length of time.[9,10] A few of our samples showed signs of deterioration (peeling off, change of color, etc.) a few months after preparation. An electron-probe analysis on such samples qualitatively showed regions containing excess of Te. The film used for the present study did not show such a deterioration. To further check the stability of the film, we measured the MCD before and after it was exposed to humidity and found a constant signal. Thus, we concluded that our film is quite stable in air. If one admits that the stability is strongly related to the stoichiometry of the sample, this would suggest that this film is very nearly stoichiometric.

EXPERIMENTAL RESULTS

The optical density D of YbTe was measured on a Cary 17 spectrometer at 300 and 10 °K (Fig. 1) between 1.85 and 5 eV. At 300 °K, in addition to the absorption bands centered around 2 eV (Refs. 2 and 11) and 3 eV (Ref. 2), we observe shoulders or steps on a continuously rising background absorption up to 6 eV. At 10 °K, the spectrum is much better resolved. The location of the absorption peaks observed at this temperature is reported in Table I. For comparison we have also included the values for YbSe[12] and YbS.[13] The MCD spectrum of the same film has been measured at both temperatures between 1.85 and 3 eV with an apparatus described earlier,[14] using a 37.5-kG magnetic field.

In the case of an isolated absorption band and assuming a rigid shift of spectral lines under the influence of the magnetic field, the MCD can be expressed as[14]

$$\frac{\Delta D}{\mu_B H D_m} = a\,\frac{df(\nu)}{d\nu} + \left(b + \frac{c}{kT}\right) f(\nu)\,,$$

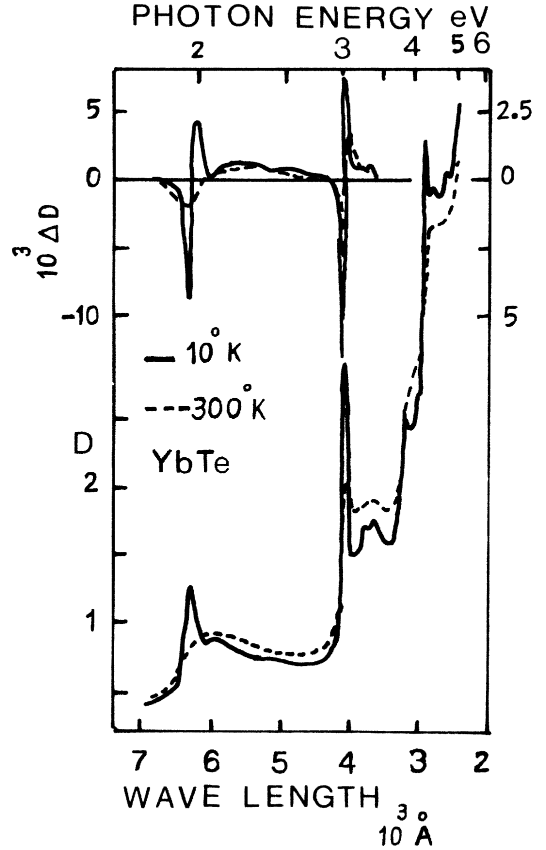

FIG. 1. Absorption (below) and MCD (above) of YbTe at 300 and 10°K. For MCD at 300°K use the scale on the right and for MCD at 10°K use the scale on the left.

where D_m stands for the maximum optical density and $f(\nu)$ stands for the shape of the band. The c/kT term only occurs in paramagnetic materials while a terms are expected for compounds possessing degenerate ground and/or excited states. The temperature dependence (Fig. 1) of the MCD indicates that all absorption bands investigated are due to a diamagnetic species, as expected for Yb^{2+}. Furthermore, the shape of the MCD for E_1' and E_2 definitely points to negative a terms. The experimental value of a was estimated to be $-1.6\mu_B$ for E_1'. For E_2, the absolute value of a is found to be slightly smaller but we think the MCD was underestimated here since the absorption was too large. The positive MCD observed between E_1 and E_2 is a clear evidence of the existence of unresolved absorption peaks in this region.

DISCUSSION

In O_h symmetry the ground state of Yb^{2+} transforms as Γ_1^+ and transitions are electric dipole allowed to Γ_4^- excited states. MCD a terms are expected for such transitions since the excited state is an orbital triplet; they can be computed from $a = -\langle \Gamma_4^- \mid L_z + 2S_z \mid \Gamma_4^- 1\rangle$, where $\mid \Gamma_4^- 1\rangle$ stands for one complex tetragonal basis of $\mid \Gamma_4^- \rangle$. Of course, for a direct comparison of theory with experiment, the configurational origin of the Γ_4^- state must be specified.

For E_1' and E_2 the sign of a is the same as that expected for a ${}^1S \rightarrow {}^1P$ transition for a free ion, as already pointed out by Starostin and Feofilov[15] in the case of a $4f^{14} \rightarrow 4f^{13}\,5d$ transition of Yb^{2+} in CaF_2.

Following the conclusions of previous papers[2,11] we assume now as a starting hypothesis that the excited states encountered in the 1.8–3.5-eV region originate from the $4f^{13}\,5d$ configuration.

We write the Hamiltonian for the excited state as

$$H = H_0 + H_{el}(fd) + H_{CF}(d) + H_{SO}(f) + H_{SO}(d) + H_{CF}(f).$$

We shall consider successively a rather crude model [Fig. 2(a)] and a more sophisticated one [Fig. 2(b)]. The former in which a weak coupling of the d electron with the $4f$ core is assumed, has already led to satisfactory results[16] in the case of Eu chalcogenides. $H_{el}(fd)$ is thus first neglected in the above Hamiltonian. Then, in O_h symmetry $H_{CF}(d)$ separates by $10Dq$ the d levels into $t_{2g}(\Gamma_5)$ and $e_g(\Gamma_3)$, t_{2g} lying lowest. In order to estimate $10Dq$, let us compare the lattice constants (a) and the ionic radii (r) of EuTe and YbTe, respectively. For EuTe, $a = 6.60$ Å and $r = 1.19$ Å; for YbTe, $a = 6.36$ Å and $r = 1.02$ Å.

TABLE I. Position of the absorption peaks of YbTe, YbSe, and YbS. Energies are given in eV.

	E_1			E_3						
	E_1'	E_1''	E_2	E_3'	E_3''	E_4	E_5	E_6	E_7	E_8
YbTe 10°K	1.97	2.09	3.03	3.28	3.38	3.86	4.08	4.24	4.38	4.73
YbSe[a] 25°K	1.75	1.85	2.95	3.11	3.31	3.88		4.35		
YbS[b] 300°K	1.62		2.80							

[a] Reference 12.

[b] Reference 13.

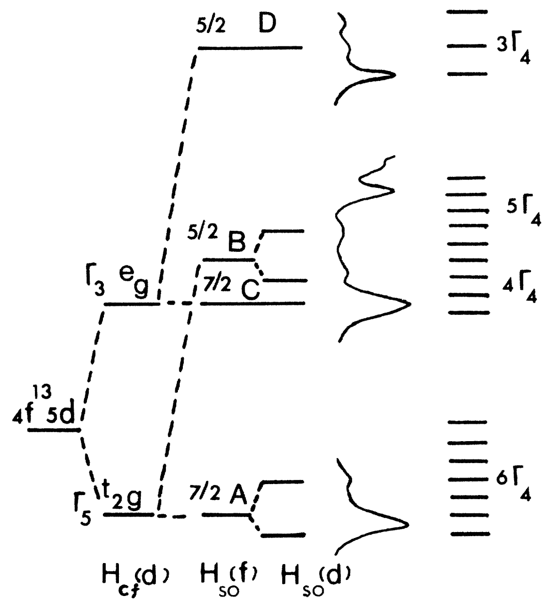

FIG. 2. Proposed energy level diagram for YbTe.

Since the experimental value of $10Dq$ is 1.55 eV for EuTe (Ref. 17) we can estimate $10Dq$ for YbTe as 0.9 eV with a point-charge model. H_{SO} (f) is obtained from the free-ion spectra of Yb^{3+} $(4f^{13})$. It results into two levels $^2F_{7/2}$ and $^2F_{5/2}$ separated by 1.24 eV (Ref. 18). Considering these two interactions alone, we thus expect the observation of four bands arising from the following transitions [Fig. 2(a)]:

$$\begin{aligned} 4f^{14}\,(^1S_0) &\rightarrow 4f^{13}\,(^2F_{7/2})\,5d\,(t_{2g}) \quad (A)\\ &\rightarrow 4f^{13}\,(^2F_{5/2})\,5d\,(t_{2g}) \quad (B)\\ &\rightarrow 4f^{13}\,(^2F_{7/2})\,5d\,(e_g) \quad (C)\\ &\rightarrow 4f^{13}\,(^2F_{5/2})\,5d\,(e_g) \quad (D)\,. \end{aligned}$$

Considering in Fig. 1 that E_1 and E_3 are separated by about 1.2 eV for YbTe (i.e., very close to the expected separation of $^2F_{7/2}$ and $^2F_{5/2}$), it is tempting to interpret these bands as due to transitions (A) and (B). We also note a similar separation between bands E_2 and E_6 and this suggests their assignment to transitions (C) and (D), respectively, as already assumed[2] in the case of YbSe. We are thus led to a $10Dq$ value (separation of A and C or B and D) of 1 eV, in good agreement with the above estimate.

This model is further supported by the fact that H_{SO} (d) only acts on t_{2g} in first order, thus accounting for the splitting of E_1 and E_3 into two components and the lack of such splitting, e.g., E_2. Finally, this model not only provides a satisfactory explanation for the gross features of our absorption spectrum but also explains in a similar fashion that of YbSe and YbS.

We now use group theory in order to show that many more levels are expected for the Yb^{2+} ion when all the terms in the Hamiltonian are considered. Considering as an example the levels arising from the lowest state (A), we take into account the spin of the d electron and the J values of the lowest $4f^{13}$ state and obtain the following direct product:

$$(\Gamma_5\times D_{1/2})\times D_{7/2}=2\Gamma_1^-+2\Gamma_2^-+4\Gamma_3^-+6\Gamma_4^-+6\Gamma_5^-$$

Thus, six fully allowed transitions are expected from the Γ_1^+ ground state. Similarly, one can establish that states B, C, and D lead to 5, 4, and $3\Gamma_4^-$ levels, respectively, as shown in Fig. 2(b). Eremin[6] has estimated the energies and intensities corresponding to these 18 transitions. Regarding the energies, a best fit between our data for YbTe and the theoretical predictions is obtained for $10Dq \simeq 1$ eV. This is very satisfactory since such a value has been computed for a point charge model. The agreement between the predicted and observed intensities is not as good however above 2.5 eV. This is not surprising since the estimate of the parameters encountered in H_{el} (fd) is very delicate and the values for the free ion might well be inappropriate. Actually, a comparison between the experimentally obtained magnetic moments for E_1' and E_2 and those computed from Eremin's wave functions would serve as a checking of these.

VALENCE-CONDUCTION-BAND TRANSITIONS

So far we have made an attempt to understand the electronic structure of YbTe on a localized model and hence nothing has been said regarding the transitions between the valence and conduction bands and the eventually associated excitonic structure. In this respect, it might be argued that the band structure of YbTe should be very similar to that of SrTe. For the latter compound, we observed, as did Zollweg,[19] an absorption peak around 3.7 eV and broader bands at higher energy; however, we did not detect any MCD with a magnetic field of 8 kG. Two conclusions can thus be reached: (i) the absorption edge around 4 eV in Fig. 1 is likely to be associated with transitions between the conduction and valence bands; (ii) the MCD measured for E_1 and E_2 is clear evidence that these are not the excitonic peaks associated with the above transition. We cannot ascertain, however, that a few features of the absorption above 3.5 eV are not due to such transitions. On the other hand, photoconductivity experiments[12,20] in YbTe (and also in YbSe) have shown that the optical absorption $4f^{14}\rightarrow 4f^{13}$ $5d$ (t_{2g}) (around 2 eV) leads to a conductive process. It might be argued that the final state of the optical excitation is the lowest conduction band. However, as it has been pointed out,[21] the excited electron can equally fall back in the 6*s* conduction band which would then be the lowest conduction band.

RELEVANCE TO SEMICONDUCTOR-METAL TRANSITION

The pressure-volume relationship[9] in YbTe, studied up to 300 kbar, shows an anomalous variation in the region 150–190 kbar though the structure remains NaCl type. This has been interpreted as due to a continuous electronic collapse with pressure, in which the Yb^{2+} ion goes over to Yb^{3+} state. Such a transition must involve the promotion of a 4*f* electron to the 5*d* state and result in a semiconductor-metal transition. Francillon *et al.*[22] have obtained, from resistivity measurements, a value of -11×10^{-3} eV/kbar for the change in the activation energy with pressure of a donor level lying 0.46 eV below the conduction band. It is assumed that this donor level is the 4*f* level of Yb. If this were true, the gap between the 4*f* level and the conduction band would close around 40 kbar. Our optical measurements[12] on a 2-μm-thick YbTe film in the infrared up to 10 μm show an absorption front around 1.8 eV corresponding to $4f\rightarrow 5d$ transition but no more subsidiary absorption bands. Assuming a value[23] of $\partial E_{opt}/\partial P = -12$ meV/kbar (similar to that of EuTe), we estimate that the gap between *f* and *d* would close around 150 kbar and not at 40 kbar, thus supporting the results of pressure-volume studies. Thus, it is possible that the donor level observed by Francillon *et al.* should be attributed to an impurity.

CONCLUSIONS

The optical absorption and magnetic circular dichroism of YbTe film has been studied at 300 and 10 °K. We have used a localized model to interpret the general features of the spectra. As in the case of Europium chalcogenides, the *f* levels of Yb are located between the valence and conduction bands. The interpretation offered for YbTe is also valid for YbSe and YbS. The MCD has enabled us to identify the diamagnetism of YbTe. That the optical properties obtained from our samples are reliable is reflected by the fact that our conclusions regarding the first absorption band due to a $f\rightarrow d$ transition are compatible with those reached from pressure-volume studies of a single crystal.

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