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Valence change of Tm in $Yb_{1-x}Tm_xS$

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The lattice constant, optical absorption, and resistivity of $Yb_{1-x}Tm_xS$ films are reported. For $0 \leq x \leq 0.18$, the samples are semiconducting and the results support the absence of a pure Tm^{3+} ground state. A semiconductor-to-metal transition takes place for $x \sim 0.2$, associated with a valence change of Tm.

Thulium monochalcogenides and their solid solutions have been examined recently in order to study the influence of valence change of Tm on different physical properties.[1] Whereas TmTe-TmSe represent a concentrated system to study Tm valence effects,[2–7] TmSe-EuSe (Ref. 4) and TmSe-YSe (Ref. 8) represent a dilute system to study such effects. In this paper we wish to report on the lattice constant a_0, optical absorption, and electrical resistivity of $Yb_{1-x}Tm_xS$ films. YbS is a diamagnetic semiconductor[9] ($f \rightarrow d$ gap ~ 1 eV), whereas TmS is an antiferromagnetic metal[10] with a Tm valence of 3. Our aim is to probe the semiconductor-to-metal transition (SMT) as a function of x and try to relate it to a change in the valence of Tm.

The thin-film samples of $Yb_{1-x}Tm_xS$ used in this paper were obtained by coevaporating Yb (Ref. 11), Tm, and S in a vacuum of 1×10^{-6} Torr onto glass and CaF_2 substrates heated to 400 °C. X-ray diffraction, electron microprobe, and secondary-ion mass-spectroscopy (SIMS) analysis were used to characterize them. In particular, the x-ray images of Yb, Tm, and S on 5-mm^2 samples showed a perfect homogeneity of the distribution of the elements with a spatial resolution better than 2 μm. All of the samples were well crystallized in NaCl structure. The variation of a_0 with x is shown in Fig. 1. If we assume a linear variation in a_0 between YbS (5.68 Å) and TmS (5.41 Å), one expects $a_0 = 5.63$ Å for $x = 0.18$. However, our samples with $x = 0.18$ had $a_0 = 5.66$ Å indicating possibly a valence less than 3 for Tm since Yb is shown to be divalent from optical data (see below). The sample BL8 with $x = 0.20$ had $a_0 = 5.61$ Å, indicating a valence very close to 3 for Tm. Though we have not explored in detail the region $0.18 < x < 0.3$, an abrupt change in a_0 seems to take place for x close to 0.2. The general conclusion that can be reached from this measurement is that Tm is neither divalent nor trivalent for $x < 0.2$.

The optical density (D) of YbS film at 10 K as a function of photon energy is shown in Fig. 2. About ten samples were examined. All of them showed two broad absorption bands near E_1 and E_2. However, only two samples showed a well-defined structure. Thus maxima were seen at 1.60 and 1.48 eV near E_1 and at 2.67 and 2.84 eV near E_2. This structure, not reported earlier by others,[9] reflects the high quality of these samples. This structure was also seen for $x = 0.02$. Following an earlier interpretation[12] of YbTe and YbSe optical spectra and noting the mean separation between E_2 and $E_1 \simeq 1.25$ eV $\simeq$ spin-orbit (so) coupling of $4f^{13}$, we assign

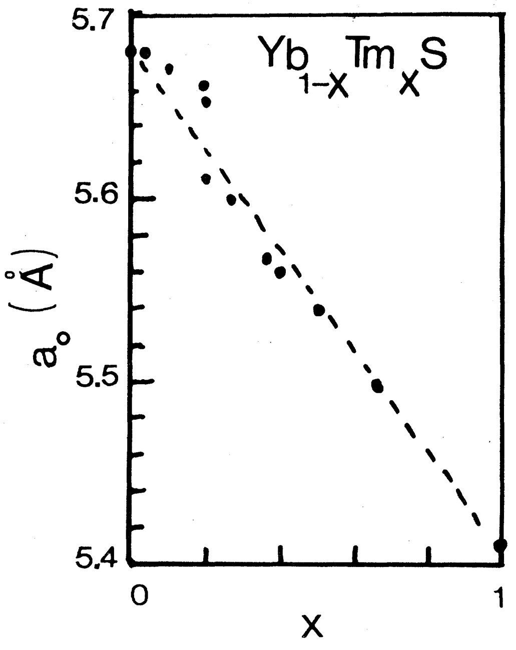

FIG. 1. Lattice constant a_0 of $Yb_{1-x}Tm_xS$ as a function of x. ●, experimental points, — — —, Vegard's law.

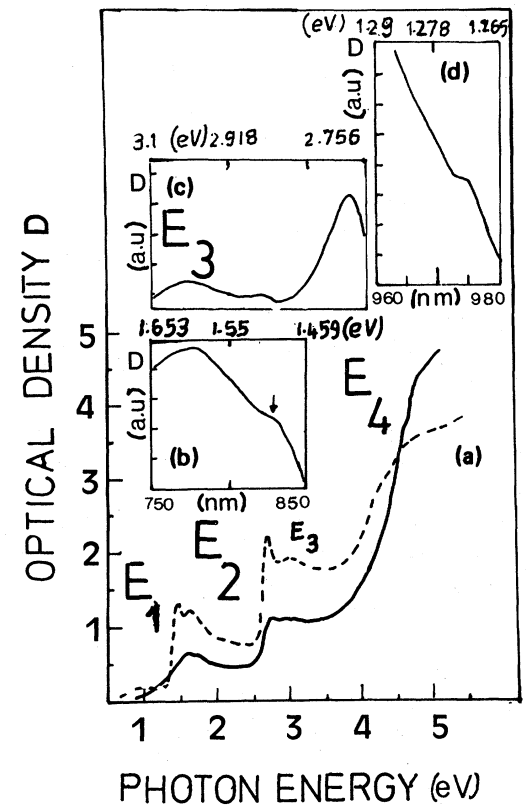

FIG. 2. Optical density D at 10 K as a function of photon energy. (a) —, YbS 0.3 μm; — — —, $x = 0.02$, 0.6 μm on CaF_2; (b) lower abscissa scale in nm, upper abscissa scale in eV; YbS 0.3 μm; (c) upper abscissa scale in eV; $x = 0.02$, 0.6 μm on CaF_2; (d) lower abscissa scale in nm, upper abscissa scale in eV; nonstoichiometric YbS; a.u. stands for arbitrary units in (a), (b), and (c).

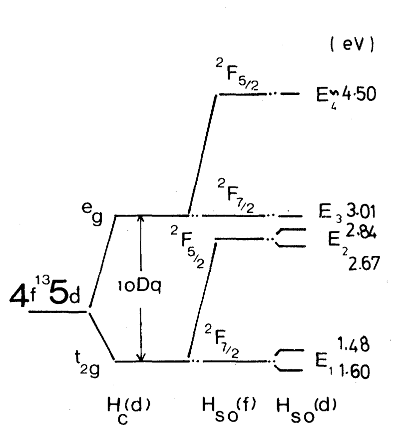

FIG. 3. Excited state configuration of $4f^{13}5d$ of YbS. Optical transitions are seen in these levels from $4f^{14}$.

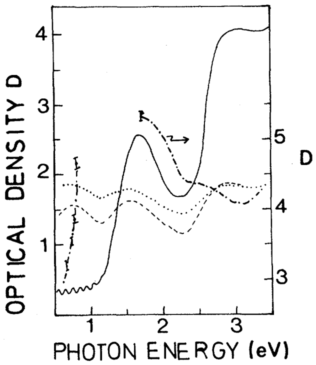

FIG. 4. Optical density D at 10 K of $Yb_{1-x}Tm_xS$ as a function of photon energy. —, $x = 0.18$, 3.2 μm, 5.66 Å; · · · ·, BL12 0.22, 0.44 μm, 5.61 Å; — — —, BL8 0.2, 0.62 μm, 5.61 Å; —·—·—·, BK20 0.65, 1.8 μm, 5.51 Å.

these bands to Yb^{2+} $4f^{14} \rightarrow 4f^{13}$ $(^2F_{7/2})$ $5dt_{2g}$ and $4f^{13}$ $(^2F_{5/2})$ $5dt_{2g}$ transitions, respectively. Then E_3 at 3.01 eV is assigned to $4f^{14} \rightarrow 4f^{13}$ $(^2F_{7/2})$ $5de_g$ giving $10Dq = 1.45$ eV. Furthermore, using the point-charge model and taking $10Dq = 2.2$ eV for EuS (Ref. 13), we estimate 1.5 eV for YbS, which is quite close to the value obtained here. The structure seen at E_1 and E_2 is explained due to the interaction of $H_{so}(d) = 0.12$ eV, which is similar[12] to that obtained in the case of YbTe and YbSe (Fig. 3). A broad maximum around 4.5 eV (E_4) can be attributed to $4f^{14} \rightarrow 4f^{13}$ $(^2F_{5/2})$ $5de_g$. One of our YbS samples showed a very weak shoulder around 1.27 eV [Fig. 2(d)] which can be interpreted as $4f^{13}f \rightarrow f$ transition indicating the presence of Yb^{3+} ions in O_h symmetry. This is attributed to deviations from stoichiometry in the cubic NaCl structure. If another phase like Yb_3S_4 were present, then we expect three peaks due to orthorhombic symmetry. Indeed, in samples obtained under different conditions and of composition close to this phase, we do observe 3 peaks between 1.33 and 1.24 eV.

The absorption bands due to Yb^{2+} transitions are clearly seen for $x = 0.02$. The maximum near 0.93 eV is attributed to an interference fringe (IF) by the following argument. The refractive index n is calculated from the IF and known thickness for other YbS samples and is used to calculate the IF maxima assuming the maximum near 0.93 eV is an IF. These are expected at 2.9 and 17 μm. The optical density (not shown here) does show a broad maximum near 3 μm and shows none till 10 μm, the limit of our measurements. Thus there is no evidence of a free carrier nor any other absorption process till 10 μm. If Tm^{3+} were present, a plasma resonance is expected around 0.43 eV which is not observed. Thus we conclude Tm^{3+} is not present in this sample. Tm^{2+} $4f^{13} \rightarrow 5d$ transitions can be expected to occur far in the infrared beyond the limit of our measurement. For $x = 0.18$, the principal absorption bands due to Yb^{2+} are clearly seen (Fig. 4). The region between 0.5 and 1 eV is dominated by IF. Again for this concentration of Tm, the presence of Tm^{3+} would lead to a free-carrier absorption near 1.35 eV which is clearly absent. Hence it is very tempting to postulate the absence of Tm^{3+} ions for $0 < x \leq 0.18$. Two samples having $a_0 = 5.61$ Å show higher absorption compared to those discussed above (Fig. 4). One of the samples had $x = 0.20$. In spite of the high absorption, Yb^{2+} transitions are clearly seen. No Yb^{3+} $f \rightarrow f$ transitions are detected. The absorption band near 1.5 eV, in particular, has broadened compared to that of YbS reflecting the broadening of the $5d$ band. This also indicates the setting in of a transition to a metallic state. The minimum at 1.15 eV is interpreted as partly due to free-carrier absorption. It is observed that the values of E_1 and E_2 are hardly affected for these values of x. The $f \rightarrow d$ transitions which are at the origin of these bands are conditioned by the immediate environment of Yb ions. It appears as though Yb-S separation does not seem to change considerably.

The optical density of BK20 ($x = 0.65$) reveals a broad shoulder near 2.65 eV which can be attributed to E_2. A minimum around 2.4 eV is followed by a steep raise. The measurements are uncertain between 1 and 1.7 eV due to very high absorption. However, there is an indication of decrease in D between 0.8 and 0.5 eV. A concentration of 65 at. % Tm^{3+} would lead to a plasma edge around 2.5 eV, in close agreement with the observation. The E_1 band is masked by the free-carrier absorption in that spectral region. When the metallic (or quasimetalic) phase is approached, more and more free (or nearly free) electrons are available in the d band for screening. It was proposed[14] that the crucial effect of the screening would be to reduce the elecron-hole interactions. Any excitonic effect would then be eliminated and no structure due to $f \rightarrow d$ transitions will be seen. However, we do see $f \rightarrow d$ transitions in the metallic phase as just shown above and hence rule out this explanation. Further, photoconductivity in this spectral region (in the semiconducting state) does not seem to suggest the presence of $f \rightarrow d$ excitons.[15]

The resistivity ρ of some of the samples have been measured using the 4-point van der Pauw method for $10 \leq T \leq 300$ K (Fig. 5). In general, two activation energies are observed: ΔE_1 for $T > 100$ and E_2 for $T < 100$. The ρ of two YbS samples range between 2 and 7 k Ω cm, whereas $\Delta E_1 \simeq 0.1$ eV, which is not very different from YbTe and YbSe films.[12] This represents an unidentified impurity level. The sample BJ20 ($x = 0.02$) has $\rho = 44$ Ω cm with $\Delta E_1 = 63$ meV and $\Delta E_2 = 25$ meV. Assuming a mobility of 1 cm^2/V sec and all Tm trivalent, we estimate $\rho = 9$ mΩ cm, which is far too small compared to the measured value. This fact, combined with the earlier discussed optical data for the same sample, indicates the absence of Tm^{3+}. One could also argue that the free carriers due to Tm^{3+} are trapped, for example, in the grain boundaries. However, the lattice constant does not suggest the presence of Tm^{3+}. On the other hand, the low ρ value compared to YbS should be related to Tm^{2+} levels lying very close to the conduction band. The sample BI8 ($x = 0.10$) had $\rho = 0.10$ Ω cm against an estimated value of 0.002 Ω cm, leading to similar conclusions as above. However, BL8 ($x = 0.20$) had $\rho = 70$ mΩ cm and BL12 ($x = 0.22$) had 2 mΩ cm with both ΔE_1 and $\Delta E_2 = 0$. The estimated value of ρ is also very close to the observed values and thus it is quite reasonable to propose that at a_0 approaching 5.61 Å there is a SMT in close agreement with the optical data.

It is thus proposed here that Tm does not prefer a pure $4f^{12}$ state in $Yb_{1-x}Tm_xS$ at least for x up to 0.18. The role played by the $5d$ band in these types

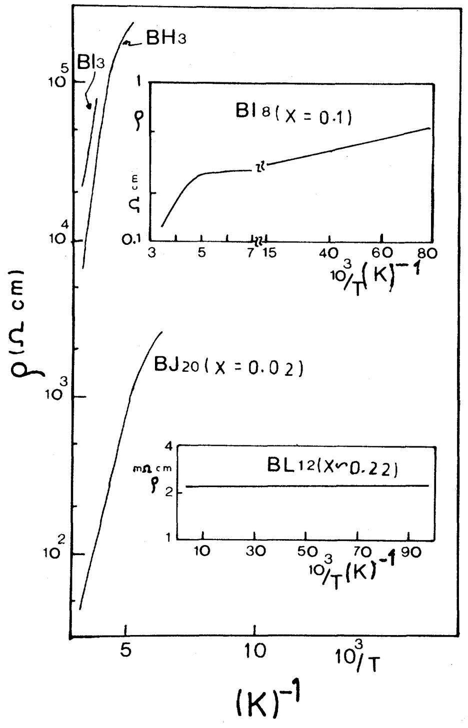

FIG. 5. Resistivity ρ as a function of $1/T$. BH3 and BI3 are YbS.

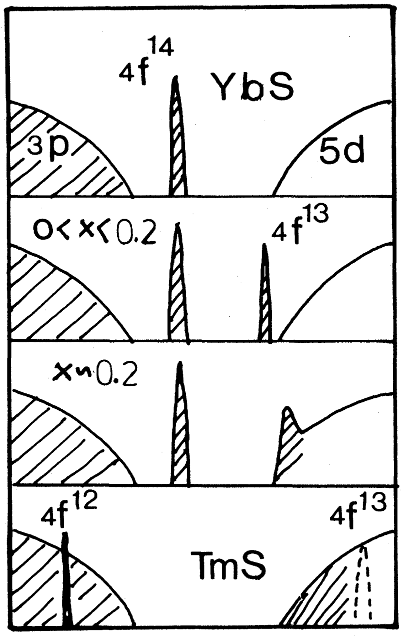

FIG. 6. Proposed electronic structure of $Yb_{1-x}Tm_xS$. 3*p* is the valence band, 5*d*-6*s* is the conduction band. 5*d* crystal-field splittings are not shown. For TmS see Ref. 18.

of materials to induce a SMT or a valence change was qualitatively discussed recently.[16] For example, in $Yb_{1-y}Sm_yS$ it was shown[16] that an increase in Yb concentration results in shifting the 5*d* band to higher energies favoring Sm^{2+} ground state for all *y*. On the other hand, in $Sm_{1-q}Tm_qS$ for very low *q* (=0.18), Tm succeeds[16] in bringing down the *d* band resulting in a valence change of Sm and in a SMT. In our case the increase in Yb concentration succeeds in shifting the 5*d* band in such a way as to push down the $4f^{13}$ of Tm just below the bottom of the conduction band. On the other hand, for increasing Tm concentration the $4f^{13}$-5*d* separation becomes smaller and smaller, finally resulting in a stable $4f^{12}$ configuration for Tm. It is interesting to note that these results were qualitatively predicted earlier,[17] though the author did not predict the dopant concentration at which a valence change would occur. Our results while verifying this prediction indicate the dopant concentration for $Yb_{1-x}Tm_xS$.

A simplified electronic structure for $Yb_{1-x}Tm_xS$ is proposed based on the results here (Fig. 6). This work, we hope, will stimulate further interest in studying transport and magnetic properties since this system could very well show properties very similar to TmSe-YSe (Ref. 8), the difference, however, being that here we have an insulating material with a mixed-valent Tm for $x < 0.20$.

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