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OPTICAL ABSORPTION OF SEMICONDUCTING AND METALLIC SmS AND Sm_{1-x}Ln_xS FILMS

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Résumé. — Nous avons étudié la transition semiconducteur-métal (SC-M) en suivant l'absorption optique due à $4f^6 \rightarrow 4f^5 5d(E_1, E_2)$ que caractérise les ions Sm^{2+} , aussi bien dans la phase semiconductrice que métallique de SmS et de $Sm_{1-x}Ln_xS$. Pour Ln = Yb, les transitions optiques E_1 et E_2 sont toujours présentes lorsque $0 \le x < 1$ en nous indiquant la stabilité de Sm^{2+} et l'absence d'une transition SC-M. Pour Ln = Tm, la définition de E_1 et E_2 disparaît au fur et à mesure que x varie de 0 à 0,30. Il en résulte alors un maximum dans l'absorption assez large autour de 1 eV qui ressemble au spectre obtenu sur la couche mince métallique de SmS.

Abstract. — We have studied the semiconductor-metal transition (SC-MT) by following the optical absorption due to $4f^6 \rightarrow 4f^5 5d(E_1, E_2)$ characterizing Sm²⁺ ions both in the semiconducting and metallic phases of SmS and Sm_{1-x}Ln_xS films. For Ln = Yb, the E_1 and E_2 transitions are well preserved for $0 \le x < 1$ showing the stability of Sm²⁺ and the absence of a SC-MT. For Ln = Tm, the definition of E_1 and E_2 disappear as x increases from 0 to 0.30 resulting in a broad maximum near 1 eV which resembles that of the metallic SmS film.

1. Introduction. — Divalent samarium sulfide undergoes an isostructural (NaCl \rightarrow NaCl) semiconductor to metal transition (SC-MT) at 6.5 kbars [1]. The metallic phase stable only above this pressure has a non-magnetic ground state [2] which is ascribed to a non-integral valency of 2.7 of Samarium. A SC-MT also takes place with cation [3, 4] or anion [5] substitution in SmS. Some models, though incomplete, have been proposed to explain these results [6a, b]. Since this SC-MT is closely related to Sm²⁺ 4f⁶ \rightarrow 4f⁵ 5d transition [1] which incidentally identifies the valence state of Sm, we have attempted here to probe the SC-MT by following the 4f⁶ \rightarrow 4f⁵ 5d optical transition both in the semiconducting and metallic phases of SmS and

$$Sm_{1-x}Ln_xS(Ln = Tm, Yb)$$

films.

2. Results and discussion. -2.1 PREPARATION. Semiconducting polycristalline films were obtained by either evaporation of the compound [7] or by co-evaporation of the elements [8] on heated CaF₂, saphire and Herasil substrates. These films showed often a preferred (111) orientation with a lattice

(*) Permanent address : A. I. Ioffe Physico-Technical Institute 194021 Leningrad, U. S. S. R. constant $a_0 = 5.965 \pm 0.004$ Å (NaCl structure). They looked green by transmission and blue or bluish black by reflection but acquired a permanent golden colour by reflection (blue by transmission) on polishing with a diamond paste [7, 9, 10]. These golden films had a_0 ranging from 5.74 to 5.69 Å (NaCl type), the latter value resembling that of the high pressure phase of SmS [1]. The Sm_{1-x}Ln_xS films were all obtained by evaporation of the individual elements [8].

2.2 OPTICAL ABSORPTION. — The optical density (and reflection in some cases) of the samples was measured with a Cary 17 spectrophotometer in the photon energy range $0.4 \le hv \le 6 \text{ eV}$ and as a function of temperature $8 \le T \le 300 \text{ K}$.

2.3 SEMICONDUCTING SmS (SC-SmS). — The optical absorption data of SC-SmS known upto 3.2 eV [11] have been extended in this study to 4.5 eV (Fig. 3a). The absorption maxima are interpreted as follows :

$$Sm^{2+} 4f^6 \rightarrow 4f^5(^6H) 5dt_{2g}$$
 (E₁)

 $4f^{5}(^{6}F) 5d t_{2g}$ (E₂)

 $4f^{5}(^{6}H) 5d e_{g}$ (E₃)

 $4f^{5}(^{6}P) 5d t_{2g}$ (E₄)

 $4f^{5}(^{6}F) 5d e_{g}$ (E₅)

based on earlier models [11, 12]. It is comforting

to note that the transitions E_1 to E_5 have also been identified in the measurements on single crystals [13] which could speak for the quality of our samples. We have tried to estimate E_g the $f \rightarrow d$ gap from the absorption curve of different samples varying in thickness from 0.2 to 3 μ . A range of values

$65 \leq E_{\rm g} \leq 350 \,{\rm meV}$

is obtained, because the absorption tail is extended to lower energies by impurities and non-stoichiometry. By selecting the lower limit of E_{g} , one concludes that $f \rightarrow d$ gap closes (¹) at 6.5 kbars resulting in a SC-MT [14] whereas by taking the higher value of E_{g} one would find that the gap does not close at the transition at 6.5 kbars. This could play a part in selecting a proper theoretical model [6c] and perhaps calls for a detailed study of the effect of non-stoichiometry on the $f \rightarrow d$ gap and on the critical pressure.

2.4 METALLIC SmS (M-SmS). — The optical density (o.d.) of a typical M-SmS film is shown in figure 1. The absorption coefficient calculated near



FIG. 1. — Optical density of a metallic SmS film ($t \sim 1000$ Å) as a function of photon energy at 300 K. The absorption coefficient is shown in the inset. (- -) Data of Pohl *et al.* (Ref. [9b]) in arbitrary units.

the peak at 1 eV taking reflection into account is 4 to 5 times that of a SC-SmS. The o.d. decreases from 6 eV to 3 eV, shows a maximum around 1 eV and decreases upto 0.4 eV. The various maxima

(1) This is obtained by considering a shift of -10 meV/kbar in the absorption curve which has been measured on thin films (though only upto 1.5 kbar) by BATLOGG, B. *et al.*, *Phys. Lett.* **49A** (1974) 13.

 E_1 to E_5 observed for SC-SmS do not show up for M-SmS.

Pohl *et al.* [9b] have also reported on the o.d. of a M-SmS film between 0.5 and 3.5 eV. They observe a flat region between 1.2 eV and 1.7 eV (Fig. 1) and a decrease in the o.d. towards the infrared. This broad maximum is quite reminiscent of an absorption due to $4f^6 \rightarrow 4f^5$ 5d transitions. A free carrier absorption, on the other hand, would have resulted in a continuous increase in the o.d. starting from 3 eV towards the infrared.

We further observe a series of maxima superposed (Fig. 2b, c) in the region $0.8 \le hv \le 1.5$ eV.



FIG. 2. — Optical density as a function of photon energy a) semiconducting SmS 300 K, b) metallic SmS 300 K magnified 10 times, c) metallic SmS 8 K magnified 10 times.

Multiple reflection can be ruled out because of high absorption involved and because these maxima do not appear in the more transparent SC films (Fig. 2a). As the temperature is lowered the o.d. generally decreases by 10 %. At T = 8K, the different maxima are better revealed (Fig. 2c). Since we do not see the multiplet ⁶H_J resolved in the first or second absorption band of SC-SmS, it is difficult of attribute the structure seen in M-SmS to the presence of such multiplets. We hope a study of the magnetic circular dichroism in these samples would be more helpful in understanding the structure.

For 2.5 < hv < 6 eV, the absorption coefficient α (Fig. 1 inset) seems to obey the relation

$$\alpha^{2/3}\simeq (h\nu-E_{\rm vc})$$

where E_{vc} is the energy gap between the valence and conduction bands. We thus obtain from two films between 800-1 000 Å thickness

$$E_{\rm vc} = 2.3 \pm 0.2 \, {\rm eV}$$

which coincides well with that estimated for the SC-SmS [14]. One obtains a similar value from the photoemission experiments on the metallic alloy $Sm_{0.81}Y_{0.19}S$ [15]. This is not surprising since in the metallic phase obtained either by pressure or by alloying, the d-conduction band is not expected to come down (relative to the p-valence band) by more than a few tenths of eV.

2.5 SC-MT IN $\text{Sm}_{1-x} \text{Ln}_x \text{S}$ AND THE STABILITY OF Sm VALENCE. — In order to probe optically the SC-MT in SmS, Pohl *et al.* [9b] applied uniaxial pressures upto 8 kbars to a SC-SmS film. However, they did not succeed in observing any change but for a small increase in the o.d. On the other hand, it would be more instructive to see the evolution of the spectrum in the alloys with Ln = Y, Gd, Tm etc., as a function of x. These alloys turn metallic for $x \ge 0.15$ [4, 5]. Indeed, for Ln = Tm and for

we observe an increase in the absorption and the definition of E_1 and E_2 vanish resulting in a broad maximum as in the case of M-SmS (Fig. 3c) (²).



FIG. 3. — Optical density as a function of photon energy: a) semiconducting SmS $t = 6\,000$ Å at 8 K, b) Sm_{1-x}Yb₈S $t = 6\,000$ Å, $x \simeq 0.65$, $a_0 \simeq 5.74$ Å at 300 K, c) Sm_{1-x}Tm_xS $t = 4\,000$ Å, $x \simeq 0.25$, $a_0 = 5.86$ Å at 300 K.

The o.d. shows a decrease from 1 eV to 0.5 eV indicating that this is not a free carrier absorption. The maxima E_3 , E_4 and E_5 seen for x = 0 are not seen for $x \leq 0.3$.

(2) For $x \simeq 0.25$, the film is blue by transmission and by reflection. For $x \ge 0.30$, the films are golden by reflection and blue by transmission.

The reflectivity of single crystals of $Sm_{1-x}Y_xS$ have been studied in detail [13]. For

$$x = 0.28 (a_0 = 5.68 \text{ Å})$$

the spectrum (measured on a cleaved golden surface) shows structure, like E_1 and E_2 , reminiscent of Sm^{2+} . For x > 0.35, the reflectivity shows a minimum between 3.2 and 3.5 eV followed by a steep increase for lower energies [13]. The o.d. being very high for x > 0.35 in our samples, we measured the room temperature reflectivity which show a minimum between 2.5 and 2.9 eV and a steep increase for lower energies.

The observed broad maximum (0 < x < 0.3) could indicate that crystal field effects become screened by the carriers in the d-band and or a broadeninig of the 4f levels of the divalent Samarium into the 5d band. This qualitative picture also supports the model proposed by T. Penney and F. Holtzberg [16] who argued for a virtually bound state formed by f⁶ and f⁵ 5d bands for the metallic phase (x = 0.2)of Sm_{1-x}Y_xS alloys. In this connection, the results of electronic Raman scattering in Sm_{1-x}Y_xS are very relevent [17]. The Raman transition identified as J = 0 to J = 1 (Sm²⁺ ground state ⁸F_J = 0, 1, ..., 6) in SmS stays unaffected in Sm_{1-x}Y_xS ($0 \le x \le 0.4$) alloys, although for these values of x, a SC-MT is observed.

For Ln = Yb, a_0 decreases continuously from 5.97 Å to 5.68 Å as x changes from 0 to 1. The films all look green by transmission though a_0 passes through a value of 5.72 Å, the critical value when a SC-MT takes place for other Ln = Y, Gd, Nd, Tm [4,5]. The optical spectra show maxima near E_1 , E_2 and E_3 which can be indentified as Sm^{2+} 4f⁶ \rightarrow 4f⁵ 5d transitions (Fig. 3b). The additional maximum seen around E'_2 falls very near the region where

or

$$Af^{14} \rightarrow Af^{13}(^{2}F) 5dt$$

 $Yb^{2+} 4f^{14} \rightarrow 4f^{13}(^{2}F_{7/2}) 5d e_{e}$

$$41^{14} \rightarrow 41^{10} ({}^{2}F_{5/2}) \text{ 3d } t_{2g}$$

is expected [18, 19]. Note that E_2 coincides with $E'_1 4f^{14} \rightarrow 4f^{13}({}^2F_{7/2})$ 5d t_{2g} [18]. This shows that Sm retains its valence state of 2 for $0 \le x \le 1$ and hence no SC-MT can be expected for Ln = Yb.

2.6 TEMPERATURE EFFECTS. — A single crystal of $Sm_{0.82}Gd_{0.18}S$, for example, changes colour from gold to black as T is reduced from 300 to 100 K accompanied by a lattice expansion and the crystal disintegrates into powder [3]. In our films for Ln = Tm, we do not observe any such disintegration or change in colour at low temperatures. It is not because we have Ln = Tm [4], for similar changes have also been observed in single crystals with Ln = Tm for a particular value of $x \simeq 0.2$ [20]. We feel either we have not obtained the critical composition or the lattice in films is in a sort of frozen state because of

its attachement to the substrate which prevents the film from cracking. Perhaps one should try hetero or homoepitaxial films.

2.7 CONCLUSIONS. — The optical absorption due to $\text{Sm}^{2+} 4f^6 \rightarrow 4f^5(^6\text{H}, ^6\text{F}) 5d t_{2g}$ transitions $(E_1 \text{ and } E_2)$ was measured both in the semiconducting and metallic SmS and $\text{Sm}_{1-x}\text{Ln}_x$ S films. For Ln = Yb, for 0 < x < 1, a_0 varies continuously from 5.97 Å to 5.68 Å and the spectra always show E_1 and E_2 indicating the stability of Sm^{2+} and an absence of a SC-MT. For Ln = Tm, for $x \le 0.3$, the spectrum resembles very much that of a metallic SmS film. It seems in the mixed valence phase, the f electrons seem to obey

atomic spectral rules, a fact which has not been taken into account by the existing theoretical models. As for the intermediate lattice constant of the metallic SmS (5.72 Å) suggesting a mixed valence for Sm, it is interesting to note that metallic SmS film with $a_0 = 5.63$ Å was recently obtained [21] whose properties should be interesting as in this case the valency of Sm is expected to be very close to three.

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