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DEGREE OF VALENCE MIXING IN THE METALLIC PHASE OF SmS AND IN TmSe

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Résumé. — Nous avons mesuré la réflectivité optique du TmSe et de la phase métallique du SmS avec des photons d'énergie entre 0,03 eV et 12 eV. Par les mesures différentielles des constantes de réseau du SmS semi-conducteur et métallique et de la fréquence des plasmons, nous concluons à une valence intermédiaire (2,85-2,9) dans la phase à haute pression. Dans le TmSe, la fréquence des plasmons révèle à peu près un électron délocalisé par ion de Tm.

Abstract. — We report about the optical reflectivity of TmSe and of the metallic phase of SmS in the photon energy range between 0.03 eV and 12 eV. From the differentially measured lattice constants of both semiconducting and metallic SmS and from the plasma frequency, we deduce an intermediate Sm-valence of 2.85-2.9 in the high pressure phase. Also in TmSe, we conclude from the plasma frequency the existence of about one delocalized electron per Tm-ion.

In the last few years, the discussion about mixed valence compounds opened a very interesting field of solid state physics [1]. Although the concept of variable valence is well known in chemistry, it has extraordinary consequences in connection with Rare Earth (RE) elements and compounds and their physical properties. As is well known, many of the RE ions appear not only in the trivalent oxidation state, but also in the divalent or tetravalent one, and the occupation number of the 4f shell changes concomitantly. In some compounds, the RE ions appear *a priori* in different valencies and the different valent ions can be situated on equivalent or inequivalent lattice sites. In the first case, the excess 4f electrons of the lower valent cation move through the cation sublattice by means of a temperature activated hopping (Sm_3S_4 , Eu_3S_4 , ...) [2-4], at least above the charge ordering transition [5], and any cation experiences a fluctuating valence, whereas in the latter case the different valencies are static and regularly distributed (Eu_3O_4 , ...) [6].

But in this paper, we are dealing with a third group of mixed valence compounds, where every cation has a hybridized configuration in the form $4f^n - 4f^{n-1}$ (5d 6s). It depends now only upon the hybridization energy relative to the energy differences between the various excited states involved in an experiment, whether one speaks of an intermediate valence [1]. Assuming a typical hybridization energy of 10^{-2} to 10^{-1} eV e. g. a Mössbauer-measurement ($\sim 10^{-6}$ eV) shows an isomer-shift corresponding to an intermediate valence, while photoemission (XPS- or UPS) measurements (~ 10 eV) detect a coexistence of two electronic configurations with integer number of 4f electrons.

One of the most important problems is to determine the degree of valence mixing. In principle, different methods seem to be appropriate, but every one has its own problems. For example, XPS and UPS compare the *intensities* of the typical 4f multiplets in the energy distribution of emitted photoelectrons, while the Mössbauer effect and the method of the *chemical shift of corelevels* [7] measure *spectral* shifts. In the latter two procedures, a simple interpolation between the frequencies of non fluctuating ionic compounds yields the degree of mixing but covalency effects are rather difficult to estimate. An other easy way is the comparison of the measured lattice constant with the limiting values expected for pure valencies. This is based on the fact, that the ionic radii of different valent RE ions change up to 10 %. The validity is restricted by both principal and practical difficulties. First of all, a *linear* interpolation seems not to be suitable, because the potential energy distribution in general is not the same for different valent ions, moreover, the lattice constant is similarly influenced also by stoichiometry.

In consequence of all these special peculiarities it is desirable to have a further instrument at one's disposal to determine the degree of valence mixing. The hybridization between $4f^n$ and $4f^{n-1}$ (5d 6s) is equivalent to a partial delocalization of an electron, or in the language of the energy band theory, a change of the effective mass m^* of the electron. The light electrons now are able to build up a common collective plasma oscillation, its frequency being given by the electron density and m^* . This coherent movement only arises, if the plasmon energy is larger than the hybridization energy. Thus, a measurable plasma resonance yields an

upper limit for the hybridization energy together with the effective mass and the density of electrons. The effective optical mass can be determined for instance with cyclotron resonance measurements.

SmS is at normal conditions a semiconductor with a narrow energy gap (~ 0.1 eV) between the occupied and localized $4f^6$ states and the 5 d conduction band. It crystallizes in the rock salt structure and Sm is divalent. Rising pressure increases the crystal field splitting of the 5 d conduction band, keeping the center of gravity constant [8], and an isostructural first order phase transition with typical hysteresis occurs [9, 10]. The metallic high pressure phase has been the subject of many investigations and from lattice constant, specific heat [11], susceptibility [12] and Mössbauer isomer shift [13], an intermediate valence has been deduced.

We obtain the golden, metallic phase by polishing black semiconducting crystals. Chemical analysis yields stoichiometry with a precision of ± 0.5 % and a comparison of the room temperature electrical conductivity ($37 \Omega^{-1} \text{ cm}^{-1}$) with systematic investigations of the el. conductivity as function of chemical composition [14] confirms the good quality of the samples used. The first experiment we have performed on such a black crystal with a golden surface, was a X-ray Bragg reflection. Surprisingly, we found two sets of reflexes with equal line width and we computed lattice constants of 5.97 \AA and 5.68 \AA , corresponding doubtlessly to the semiconducting and the metallic phase. Moreover, this important result shows, that the surface is single crystalline and it supports our measurements as being representative for single crystals under hydrostatic pressure. This experiment has the additional advantage of every differential method and is free of calibration problems. Now we are able to estimate the degree of valence mixing using the new lattice constant of 5.68 \AA . In absence of a better way, also we interpolate linearly between the expected value of the Sm^{3+}S and the known one of Sm^{2+}S and obtain an intermediate valence of 2.85 for Sm. However, in a recent work on SmS films it is reported about the existence of SmS films with every lattice constant between 5.62 \AA and 5.97 \AA [15].

As mentioned above, the plasma resonance of the light electrons gives information about the degree of valence mixing. We have measured the reflectivity of the metallic phase of SmS in the photon energy range between 0.03 eV and 12 eV , and in function of temperature (4.2 K to 300 K). The spectrum in figure 1 behaves *normal* as known from Gd- and La chalcogenides [15] with interband transitions above 3 eV and plasma oscillation below 3 eV . On cooling to 4.2 K , the reflectivity edge, producing the golden colour, remains at the same energy and becomes only somewhat steeper as expected. In contrast, the reflectivity edge in chemically collapsed $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ shifts toward lower energies with decreasing temperature [17] and this is the first decisive hint that chemical alloying is not equivalent to external mechanical

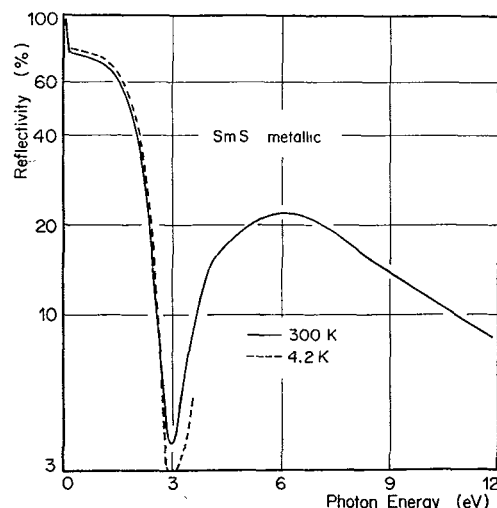


FIG. 1. — Optical reflectivity of metallic SmS at 300 K (full line) and at 4.2 K (dotted line).

pressure alone. By means of a Kramers-Kronig analysis, we derived the complex dielectric function $\epsilon_1(\omega) - i\epsilon_2(\omega)$. The real part increases from very large negative values at low energy and crosses the real axis at 2.45 eV . The positive slope of ϵ_1 and a maximum in the energy loss function $\epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$ at this energy (Fig. 2) indicate a longitudinal excitation mode, the coupled plasmon mode. The interaction between the free electrons is slightly screened by the presence of interband transitions and the unperturbed resonance will be shifted to higher energy.

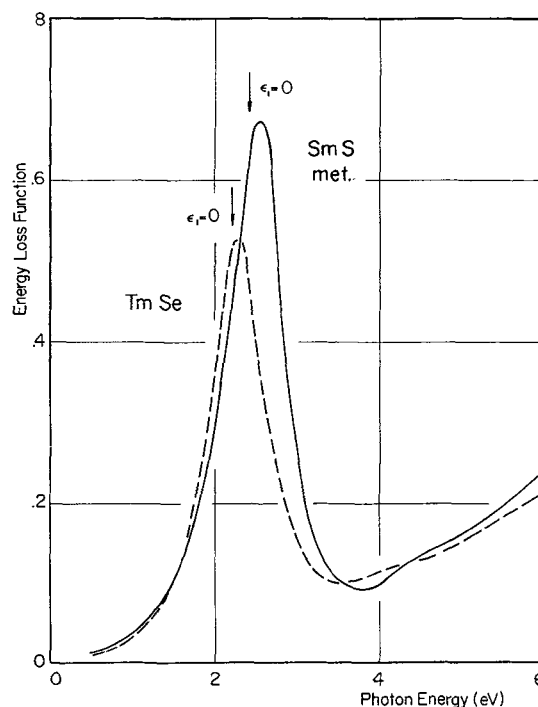


FIG. 2. — Energy loss function of metallic SmS and of TmSe.

With a procedure described elsewhere [18], we decompose ε_1 into contributions from bound ε_1^b and free carriers ε_1^f . Now, the intersection point of ε_1^f with the real axis at 4.6 eV gives the energy of the unperturbed plasma frequency ω_p of the conduction electrons. Because ω_p , the density of carriers N and the effective mass m^* are connected by

$$\omega_p^2 = 4 \pi N e^2 / m^*,$$

we can immediately derive the number of light electrons per cation. Many other similarities in the electronic structure encourage us, to assume the same light effective mass in GdS ($m^* = 1.3 m$) [16], because it is the same band with nearly the same degree of filling.

Using the relation above, we obtain 0.9 electrons with $m^* = 1.3 m$ per Sm and an intermediate valence of 2.9. The agreement with the value deduced from the differentially measured lattice constant is satisfactory.

The intermediate valence of Sm in pure SmS, determined on single crystalline samples with stoichiometric composition therefore is doubtless *higher* (2.85-2.9) than in chemically collapsed systems (2.7). Also the isomer shift measurements by Coey *et al.* [13] on high pressure SmS and on $\text{Sm}_{0.77}\text{Y}_{0.23}\text{S}$ clearly show a difference in the spectra and confirm, that chemical doping is not equivalent to external pressure alone.

The story about the Tm-monochalcogenides is extremely complex and is characterized by experimental results not giving a uniform picture [19]. We get a first survey comparing their lattice constants with other RE chalcogenides. TmTe evidently belongs to the divalent and TmS to the trivalent ones. Consequently TmSe is expected to be in an unstable situation with respect to the valence state and every perturbation, intended or not, changes the equilibrium. This inherent problem renders it impossible to speak about the properties of *the* TmSe. Most experiments are performed on different samples and as soon as we accept a slight variation of the composition as a triggering factor of the valence state, it is not sufficient to give only the lattice constant of the sample investigated. On the contrary, exact characterizations of the substances are desirable and necessary, albeit it is laborious, but the solution of the Tm-chalcogenides-problem strongly depends on this point.

In this part, we report about the optical properties of TmSe with respect to valence mixing. The 4f shell of Tm in the divalent state is occupied by 13 electrons, in the trivalent one by 12. Thus, a possible hybridization occurs between $4f^{13}$ and $4f^{12}$ (5d 6s). The collective mode of light electrons, as explained in connection with SmS, moves in a coherent manner and one should observe a plasmon oscillation, if only the hybridization energy is less than the plasmon energy.

Already the first sight gives evidence of the metallic nature of TmSe, its lustrous copper colour is well known from the Gd- and La chalcogenides. We have

measured the reflectivity of single crystals in the same photon energy range as SmS. The result, given in figure 3, confirms the first impression of the naked

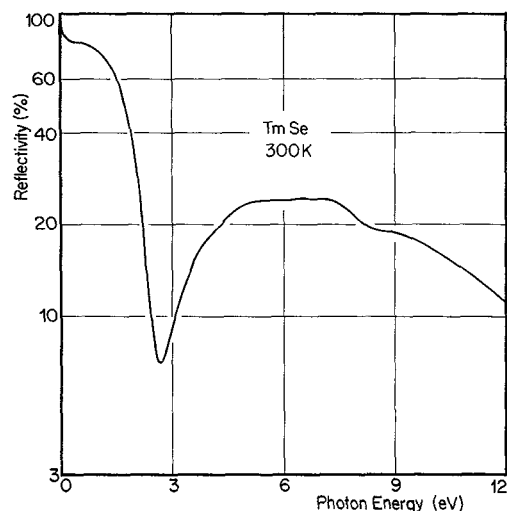


FIG. 3. — Optical reflectivity of TmSe at 300 K.

eye: interband transition at higher energies and a plasmon characteristics at lower energies. For detailed discussion of the spectrum see ref. [20]. With the same analysis and decoupling procedure as in SmS, we first prove the longitudinal nature of the collective mode and in figure 2, the sharp resonance in the energy loss function is obvious. It is important to observe such a plasma oscillation in TmSe and assuming the same effective mass as in GdSe ($m^* = 1.65 m$), the calculation yields about one free electron per Tm ion equivalent to an *intermediate valence* close to 3. In this connection, we want to draw the attention not especially on the exact number but more on the existence of the collective resonance of free carriers with reasonable density and usual effective mass.

A severe discrepancy exists between the reflectivity in the middle infra-red (~ 0.1 eV), reported by Ward *et al.* [21] ($\sim 7\%$) and ours ($\sim 80\%$). These authors explain their results also with plasmon oscillations, but are forced to assume a very high effective mass (~ 1000) and attribute it to valence fluctuation. A comparison of the lattice constants doesn't bring any solution. The *intermediate valence* of our TmSe ($a_0 = 5.68 \text{ \AA}$, chemical composition: $\text{Tm}_{0.98}\text{Se}$) as deduced from a linear interpolation of the lattice constant is with 2.82 lower than in the sample of Ward *et al.*, where from $a_0 = 5.64 \text{ \AA}$ a mixed valence of 2.95 results. In a simple picture, we would expect less free electrons in our material. The reflectivity of other TmSe crystals with excess of Tm or Se differs mostly in the known dependence of stoichiometry, but the qualitative behaviour especially in the IR, does not change.

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