Low-energy electronic structure of intermediate-valence "golden" SmS

G. Travaglini and P. Wachter
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, 8093 Zürich, Switzerland
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Reflectivity measurements in the far-infrared region at 9 K show that the Fermi level of the intermediate-valence high-pressure phase of SmS lies in a gap of about 7 meV in width. At low temperatures the reflectivity has a double peak around 20 meV which is associated with intra-$4f$ transitions. The optical constants are calculated from a Kramers-Kronig analysis of the reflectivity. An oscillator fit was made that separates f-f from f-d transitions. The interband density of states was estimated for the giant f density of states to be about 1200 states per rydberg and cell compared with a density of about 70 d states per rydberg and cell. For the first time a fine structure in the density of f states has been observed.

INTRODUCTION

It is more and more generally appreciated that the ground-state properties of an intermediate-valence (IV) material are required to understand the thermodynamic behavior such as the temperature dependence of the electrical resistivity, of the magnetic susceptibility, or of the specific heat. However, there is practically no knowledge of the electronic structure of the ground state, i.e., of occupied and empty states in the vicinity of the Fermi energy E_F. Information about the electronic structure is believed to be obtained by measuring the ultraviolet photoemission (UPS), x-ray photoemission (XPS), or core-level spectroscopy. However, it is well known that these techniques measure final-state effects. With the theory of Gunnarsson and Schönhammer,[1] one can nevertheless compute the f occupancy and the f-d hybridization Δ (for Ce, $\Delta=0.1$ eV) from these measurements, but since $\Delta=\pi V_{\rm mix}^2\rho(E)$ (Ref. 2) and the mixing matrix element $V_{\rm mix}$ generally is not known, the density of states $\rho(E)$ near E_F also remains unknown. On the other hand, we seem to be sure that we have to expect large density-of-states peaks at E_F in order to explain the giant γ values which most of these materials exhibit.[3] The high-energy spectroscopies mentioned above are thus not able to characterize features within the meV range around E_F, which are the most important properties of the electronic structure.

It thus came as a surprise to many workers in the field that intermediate-valence compounds such as SmB_6, high-pressure SmS, TmSe, some $TmSe_{1-x}Te_x$ alloys, and YbB_{12} (Refs. 4–8) have a gap of order meV in the density of states and that E_F is in the gap. These materials thus have a semiconductorlike resistivity. The gap is a consequence of the f-d hybridization, and it has dramatic effects on the specific heat and the susceptibility.[9–11] It is thus of fundamental importance to know the electronic structure of the ground state in the vicinity of E_F.

There is of course no spectroscopy which can probe ground-state properties since any measurement transfers energy to the system. Soft spectroscopies, however, which use energy transfers less than the binding energy of the hybridized state (typically 10 meV), have the potential to investigate the electronic structure within meV of the ground state. Such measurements are the Mössbauer effect, point-contact spectroscopy, Raman effect, neutron scattering, and far-infrared spectroscopy.

The far-infrared reflectivity of the archetypal SmB_6 has recently been measured at ambient temperature and at 4 K (Ref. 12) and analyzed with respect to the dielectric functions. The density of states could be computed and, besides the observation of a gap of about 4 meV, for the first time evidence has been given of a large interband density-of-states peak with f character, having 11 000 states per rydberg and cell and a width of about 3 meV, situated a few meV below E_F. For comparison the density of d states amounts only to about 50 states per rydberg and cell, being spread over nearly 1 eV. (In Ref. 12 a factor 4π was lost in the values quoted for the interband density of states. They are thus 4π times larger.)

SmB_6 was chosen as the first IV material to be measured by this technique because it is IV at ambient conditions, and a large single crystal was available. For SmS one needs external pressure in excess of 6.5 kbar,[13] and for TmSe the gap is expected to be rather small [about 2.3 meV (Ref. 5)] and the temperature has to be less than $T_N\approx 3$ K.[14] We have nevertheless undertaken a study of SmS, due to the fact that one can achieve the high-pressure phase by simply polishing the surface, transforming it to the golden phase.[15,16] We are well aware that this is not the best of all conditions, but a high-pressure measurement at helium temperatures and down to 10 cm^{-1} will not be possible in the immediate future. On the other hand we must show that the large density-of-states peaks above and below E_F are not a unique feature for SmB_6 but a common behavior of a whole group of IV compounds. We thus have measured the reflectivity of gold SmS at different temperatures and analyzed it in terms of the dielectric functions.

REFLECTIVITY MEASUREMENTS

The reflectivity has been measured with three spectrometers over more than four decades of photon energy (1 meV–12 eV), and also at helium temperatures on large

single crystals. Part of the spectrum has already been published.[16,17] The high-pressure, golden phase of SmS was obtained by mechanically polishing the surface with 1-μm diamond abrasive. It is known that this treatment produces about a 10 000-Å-thick metallic layer which is thicker than the penetration depth of light.[17] Microscopic investigation of the surface revealed that it contained about 15% of untransformed, black SmS. Thus the reflectivity of black, semiconducting SmS has also been remeasured in the same wavelength and temperature range. These results agree reasonably well with the recently published data on semiconducting, black SmS.[18]

Since the polished, golden SmS surface with its 15% black spots of size between 20 and 100 μm acts like a heterogeneous mixture of two compounds the reflectivity of both fractions is additive. We thus have calculated the optical reflectivity of a 100% golden surface from the following equation:

$$R(\mathrm{SmS_{golden}}) = 1.18[R(\mathrm{SmS_{mix}}) - 0.15R(\mathrm{SmS_{black}})]$$

The reflectivity obtained in such a way is shown in Fig. 1 at ambient temperature and at 9 K. The reflectivity at high energies is dominated by a peak at about 6 eV, which has been assigned[17] to interband transitions from the $3p^6$ anion valence band to empty d conduction-band states above E_F. The reflectivity minimum at 3 eV is caused by a screened plasma resonance of carriers in the conduction band. The unscreened plasma resonance has been computed to be at 4.6 eV.[17] The steep rise of the reflectivity between 1 and 3 eV—the plasma edge—is another manifestation of the resonance of the free carriers. As can be seen from Fig. 1 these features are practically temperature independent despite the fact, as will be shown below, that a gap in the meV range opens up at low temperature: The plasma resonance is so much larger in energy than this meV gap that it does not have any influence on the reflectivity.

The main aspects of the reflectivity to be discussed in this paper are in the infrared and far-infrared energy range, and here the main feature is the structure at about

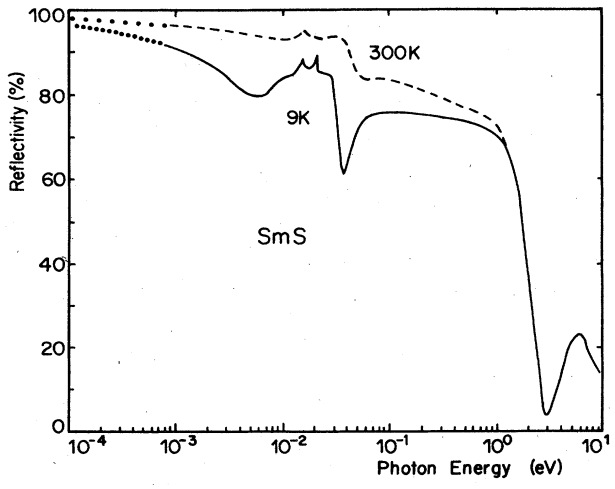

FIG. 1. Reflectivity of IV golden SmS at ambient temperature and at 9 K. The dotted curve is the extrapolation $\omega \to 0$.

20 meV. A similar structure was observed in the low-temperature reflectivity of SmB_6 at 5.5 meV, far below any possible optical phonon energies.[12] For golden SmS, however, multiplet excitations within the $4f^5$ or $4f^6$ configuration or phonon energies coincide with this far-infrared reflectivity peak at 20 meV.

As a first step we must clarify whether part of the reflectivity structure near 20 meV can be caused by uncompensated residuals of the ω_{TO} reflectivity peak at 26 meV of semiconducting, black SmS when computing the reflectivity of golden SmS. We have been very careful in eliminating this possibility: Since the reflectivity of the black phase especially at low temperatures is of the same size as the one of the golden phase, the relative corrections are less than 1%.[18]

Second, intra-$4f^5$ or intra-$4f^6$ transitions are not infrared active and generally they cannot be seen in reflectivity spectra. An assignment of a reflectivity peak at 12.5 meV of semiconducting, black SmS to a $^7F_0 \to {}^7F_1$ transition[18] is incorrect. At low temperatures the transition is found with Raman effect at 30.5 meV.[19] Also in semiconducting SmSe and SmTe the low-temperature reflectivity spectrum reveals no intra-$4f^6$ transition.[20] These transitions, however, are Raman active and their transition energies in semiconducting compounds are well known.[19] It is also known, however, that with stronger f-d mixing the Raman intensity diminishes and in IV golden SmS the intra-$4f$ transitions could no longer be observed. On the other hand they become increasingly infrared active with strong f-d mixing. It is thus not impossible that they can be observed in a reflectivity spectrum on IV golden SmS. Increased f-d mixing results in a softening of the $^7F_0 \to {}^7F_1$ transition energy[19] and the lowest observed energy for this transition is near 200 cm^{-1} or 25 meV (Ref. 21) in strongly mixed $Sm_{0.25}Y_{0.75}Se$. We thus can expect this transition also near 25 meV in IV golden SmS.

Third, it is in principle possible to observe TO phonons in reflectivity in "bad" metals, i.e., in those in which the reflectivity generally is not too high. A very good example is US (Ref. 22) and possibly also $CePd_3$.[23] Unfortunately the TO(Γ) mode in IV golden SmS, the only one to show up in reflectivity, is not well known. Inelastic neutron scattering has been performed on chemically collapsed $Sm_{0.75}Y_{0.25}S$ and $\omega_{TO}(\Gamma)$ was found to be 32 meV,[24] in agreement with a theoretical calculation.[25] On IV golden SmS only Raman scattering results on polished surfaces exist.[26] These experiments yield a phonon density of states. Taking the low-energy end of the optical band as the lower limit of the TO(Γ) energy we find 30 meV. We realize from Fig. 1 that a high-energy shoulder of the 20-meV reflectivity structure is exactly at this energy; thus we think it possible that TO phonons are involved in this structure. The reflectivity peaks at 16 and 22 meV, instead, are attributed to electronic transitions or polarons (see below).

KRAMERS-KRONIG TRANSFORMATIONS

The reflectivity spectrum of IV golden SmS has been analyzed in terms of optical constants by means of the

Kramers-Kronig relations. A conventional extrapolation of the reflectivity above 12 eV has been made.[17] Below 1 meV and for $\omega \rightarrow 0$, the reflectivity has been extrapolated (dotted curve in Fig. 1) to be compatible with the measured dc conductivity[27,28] according to the Hagens-Rubens relation. Figure 2 shows the real (ϵ_1) and the imaginary (ϵ_2) part of the dielectric functions for $T=9$ K. Regarding ϵ_2, we can separate the spectrum into three main regions below the interband transitions around 6 eV for which ϵ_2 is approximately 4.9: a broad peak around 0.2 eV, a very intense and sharp peak with fine structure around 20 meV, and an increase of $\epsilon_2 \rightarrow \infty$ for energies less than 7 meV. ϵ_1 reaches values of more than 600 in the 20-meV region and flattens off to a static dielectric constant of 230 between 1 and 5 meV. Near and below 1 meV it drops to very large negative values. It is clear from Fig. 2 that we have a gap at 7 meV, as corroborated also by the flat part of the dielectric constant ϵ_1 in the meV range. Since 9 K corresponds to about 1 meV, it is obvious that we have also an appreciable amount of thermally excited free carriers above the gap.

The most recent resistivity measurement on IV golden SmS yields at 4 K a value of only 2.3 mΩ cm,[28] so that appreciable free-carrier absorption must be expected. The gap of 7 meV is in agreement with a 6.4-meV gap obtained by point-contact spectroscopy[6] on the same sample and it is at variance with GaAs tunnel spectroscopy where 1.7 meV has been reported.[7] In Fig. 3 the absorptive and refractive indices are shown at 9 K. In the absence of free-carrier absorption the refractive index would be 17 below 7 meV. In Fig. 4 finally we show the real part of the optical conductivity on a log-log plot. Again the gap at 7 meV is obvious, but σ_1 extrapolates reasonably well to the experimentally measured dc values.[27,28]

Comparing IV golden SmS with SmB_6,[12] one realizes that the main features are the same: In SmS all transition energies are shifted to higher energies and the peaks are broader. The peak around 20 meV shows some fine structure which was absent in SmB_6 (the experimental resolution of the spectrometer is far better than any of the fine structures shown: 1 cm$^{-1}=10^{-4}$ eV). Despite the larger gap of SmS compared to SmB_6, the dc conductivity at low temperatures is orders of magnitude larger in SmS than in SmB_6.

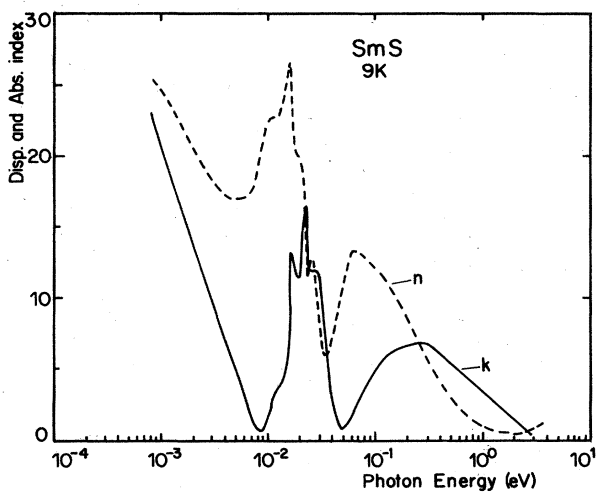

FIG. 3. Absorptive and refractive index of IV SmS at 9 K.

TRANSITION ASSIGNMENT

In the following we will discuss the transitions centered around 20 meV and 0.2 eV. We proceed along the lines given in Ref. 12 where the hybridization model of an IV material is used.[9–11] Two very large but narrow density-of-states peaks are predicted by this crude model, separated by a hybridization gap of the order of meV. The hybridization is between a $4f$ state and a $5d$ band; the degree of valence mixing can be taken from the lattice constant[14] or the Mössbauer effect,[29] and it is taken to be 2.8. The

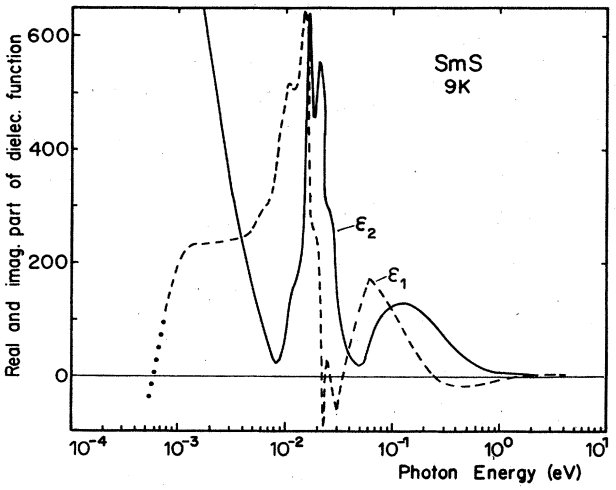

FIG. 2. Real and imaginary part of the dielectric function of IV SmS at 9 K. The dotted part is the extrapolation $\omega \rightarrow 0$.

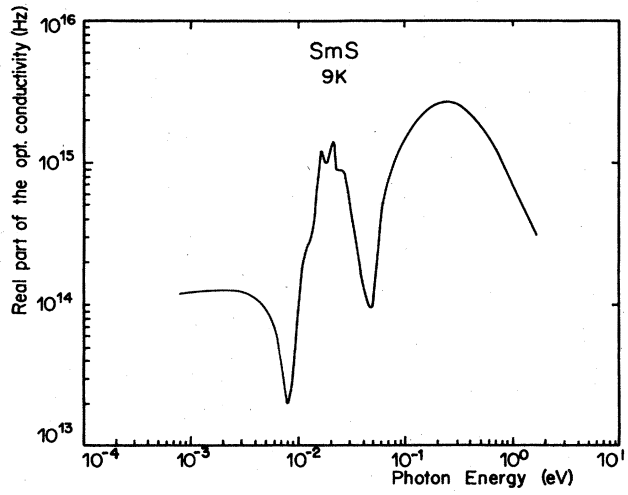

FIG. 4. Real part of the optical conductivity of IV SmS at 9 K.

lowest energy absorption, starting at about 7 meV, will thus have f-f character (parity forbidden for direct optical transitions); the second transition centered at about 0.2 eV will have a d-f matrix element. That the f-f transition nevertheless has such a strong absorption coefficient ($K \approx 4\times 10^4$ cm^{-1}) is due to the f-d mixing (enhancement of about 10^3).

Quite a number of collective oscillations of carriers (plasma resonance) can be found in Fig. 2. They are defined by $\epsilon_1=0$ and $(d\epsilon_1/d\omega)_{\epsilon_1=0}>0$. The one at highest energy is at 2.45 eV and at ambient temperature there is only one other zero crossing of ϵ_1 with positive slope at 25 meV. For lower energy ϵ_1 remains negative. Both intersections have been observed before.[17,30] Since kT at ambient temperature is large compared with the hybridization gap the materials act like metals. The two zero crossings of ϵ_1 with positive slope thus correspond to two coupled plasma resonances of light (d) and heavy (f) electrons. Since their resonances are so far apart, the intersection $\epsilon_1=0$ practically yields the eigenfrequencies of the uncoupled oscillators. The frequency of the zero crossings $\omega_p^2=4\pi eN/m^*\epsilon_{\rm opt}$ can be used to compute the effective masses m^*. From the degree of valence mixing, 2.8, we expect $N_f\approx 0.2$ and $N_d\approx 0.8$ per Sm atom and we obtain $m_d^*\approx 1.3\pm 0.1m$ and $m_f^*\approx 100\pm 50m$ using the appropriate $\epsilon_{\rm opt}$ from Fig. 2, being due to p-d or d-f interband transitions. The zero crossing of ϵ_1 with negative slope at 0.225 eV corresponds to a transverse excitation, and it yields the resonance frequency of the d-f (or f-d) transition.

At low temperatures we observe additional zero crossings of ϵ_1 near 20 meV. The signature is typical for a plasmon—LO-phonon coupling (plasmaron),[31] which seems to influence also the TO-phonon frequency (we will discuss these effects in more detail below). A last zero crossing of ϵ_1 with positive slope can be extrapolated to be at approximately 5×10^{-4} eV, and it yields the plasma frequency of the thermally excited carriers across the gap. From this resonance and with $\epsilon_{\rm opt}=230$ we obtain $Nm/m^*=4.13\times 10^{16}$. There exists a Hall-effect measurement in the high-pressure phase, but only down to 78 K:[32] R_H amounts to 4×10^{-2} cm^3/C. The measured resistivity increase between 78 and 9 K is approximately a factor of 10 (Ref. 27), and by attributing this increase to a freezing out of carriers we can estimate R_H at 9 K to be about 4×10^{-1} cm^3/C. For the analysis of the Hall effect we must of course use a two-band model, but it has been shown that the one-band model yields the upper limit of carriers.[33] Thus at 9 K, $N\leq 1.5\times 10^{19}$ cm^{-3} and we obtain $m^*\leq 360m$, again a typical f effective mass. We thus have obtained two bands with f character that have effective masses on the order of hundreds of times the free-electron mass and which are separated by a gap of 7 meV. The use of the effective-mass terminology does not imply that we neglect multielectron states, but the resonances obtained with a Kramers-Kronig analysis are one-electron resonances. Thus we project the "true" physics into the one-electron approximation. In this approximation high effective masses correspond to very narrow bands. There is, however, one clear distinction: When the bands become so narrow that the overlap between the wave functions vanishes—when the states get localized—then there is no longer a plasma resonance. This can be experimentally verified with the localized $4f^6$ states in semiconducting SmS, SmSe, and SmTe, where at low temperatures no plasma resonance exists, in spite of the fact that the $4f$-electron concentration is of the order of 10^{22} cm^{-3}.

DISCUSSION

For the discussion of the low-temperature physical properties of IV golden SmS we want to concentrate now on the two main absorption peaks near 0.2 eV and 20 meV as shown in Fig. 4. The peak near 0.2 eV (d-f transition) can be fitted with a single oscillator

$$\sigma_1=\frac{1}{4\pi}\omega\epsilon_2=\frac{Ne^2f}{m}\frac{\Gamma\omega^2}{(\omega_0^2-\omega^2)^2+\Gamma^2\omega^2}\ .$$

Here f is the oscillator strength and $\Gamma/2\pi$ the full width at half maximum. If we use the maximum value of the optical conductivity, $\sigma_{1_{\rm max}}$,

$$\sigma_{1_{\rm max}}=\frac{Ne^2f}{m\Gamma}\ ,$$

we can compute the oscillator strength f from this formula, given the experimental values $\sigma_{1_{\rm max}}$, Γ, and N. The latter must be multiplied by 0.8, the fraction of d electrons in SmS, if we assume this transition to originate in the band with mainly d character. The oscillator strength is found to be $f_d=0.368$, typical in magnitude for an allowed transition (Table I).

The transitions centered near 20 meV are shown in an enlarged and linear scale in Fig. 5. Three main maxima can be distinguished. The important question is whether these are all f-f transitions or whether phonon and multiplet transitions are also involved. The highest energy

TABLE I. Transition energy, intensity, half-width, and oscillator strength of possible transitions. Also shown is the interband of states $2J_{cv}$.

Peak position (eV)	$\sigma_{1_{\rm max}}$ (Hz)	$\frac{\Gamma}{2\pi}$(FWHM) (Hz)	f	$2J_{cv}$ (states per rydberg and cell)
0.225	272×10^{13}	6×10^{14}	0.368	69.9
0.0213	132×10^{13}	2×10^{13}	0.023	542.9
0.0185	132×10^{13}	9×10^{12}	0.010	1253.4
0.0160	120×10^{13}	3.3×10^{12}	0.0036	3480

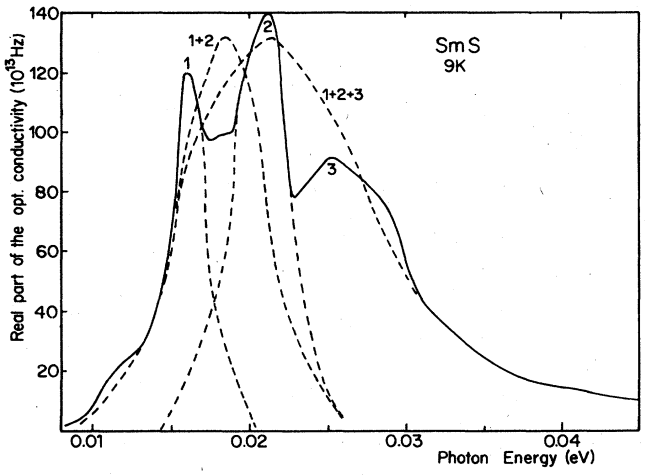

FIG. 5. Real part of the optical conductivity near 20 meV and at 9 K. Note the linear scale. Dashed curves and numbers refer to different oscillator fits (Table I).

peak centered at 25 meV has a shoulder at 29 meV which coincides in energy with the TO-phonon frequency for IV golden SmS derived above. It is also this energy where ϵ_1 indicates by its zero crossings the coupled phonon-plasmon mode. We thus attribute the high-energy shoulder at 29 meV to ω_{TO}. The peak position at 25 meV coincides with the $^7F_0$-$^7F_1$ transition, softened because of d admixture[21] and becoming allowed for the same reason. Thus the whole high-energy peak is not considered to be part of the f-f transitions.

We are left with two peaks at 16 and 21 meV. Because we do not have any means to distribute the number of electrons N over these two transitions, we construct a single peak, centered at 18.5 meV with the same area as the two peaks together and thus compute the oscillator strength with the equations above. The result is $f_f=0.01$ (Table I), using the $4f$ occupation number 0.2 as derived from the degree of valence mixing. This is a typical magnitude for a forbidden transition. A pure intra-$4f$ transition as in isolated rare earths would have, however, an oscillator strength of only 10^{-6}. The increase in oscillator strength in SmS is thus due to the d admixture when forming the IV state. As a novelty compared to SmB_6 (Ref. 12), we realize in any case that the intra-$4f$ transitions show a fine structure.

Since we cannot be absolutely certain that the highest energy peak at 25 meV is really due to other than intra-$4f$ transitions we have substituted all three peaks near 20 meV with a single oscillator at 21.3 meV and calculated the oscillator strength in the above way. The result is $f_f=0.023$, again a forbidden transition with strong d admixture (Table I). For the sake of completeness we compute also the oscillator strength for the transition at lowest energy alone (16 meV) which amounts to $f_f=0.0036$ (Table I).

The most important aspect of an IV material in order to understand its thermodynamic behavior is its electronic structure within meV of E_F. The knowledge of the dielectric function and the oscillator strength for the low-energy transitions permits us to derive the joint density of states J_{cv_i} of the ith oscillator. Thus,

$$\epsilon_{2_i}(\omega)=8\left[\frac{\pi e}{m\omega}\right]^2 |p_{cv}|_i^2 J_{cv_i},$$

provided p_{cv} is k independent, and with

$$|p_{cv}|_i^2=\tfrac{1}{2}m\hbar\omega f_i$$

we obtain

$$J_{cv_i}=\frac{\sigma_{1_{\max_i}} m}{f_i \pi e^2 \hbar}.$$

The values for the interband density of states $2J_{cv}$ for d-f and f-f transitions are shown in Table I. It now becomes clear that the density of states of f states is 10 to 50 times larger than that of the d states. As in Ref. 12, one word of caution is appropriate. The analysis of J_{cv} implies direct transitions, whereas the hybridization model demands an indirect transition for the onset of the f-f transition (Γ-X). The oscillator strength of an indirect transition is less than that for a direct transition so the quoted values of J_{cv} for the f-f transitions are lower limits only. The above-mentioned factors between the J_{cv} for f and d are not as large as in SmB_6,[12] where they are more than 100, but in general IV golden SmS also corroborates the hybridization model with two large density-of-states peaks with mainly f character separated by 7 meV and having a width of about 6 meV. The states with mainly d character extend over nearly 1 eV.

In comparison to SmB_6 we would conclude that in IV SmS the f-d mixing is stronger. This is to be expected theoretically since, with on-site mixing being forbidden, the f-d mixing depends on the Sm-Sm distance which is 4.02 Å in IV SmS and 4.13 Å in SmB_6. The larger f-d mixing is also indicated experimentally by the larger oscillator strength of the f-f transitions, their larger width, and two phenomena which were absent in SmB_6. First, in Fig. 4 the optical conductivity has a sharp minimum at about 5×10^{-2} eV which separates the f-f from the d-f transitions. This minimum leads to a drastic reduction of the density of states at that energy. However, this is exactly what is to be expected from a strongly f-d mixed material: A so-called spectral repulsion term exists as calculated for the strongly hybridized US.[34] Second, the fine structure of at least a doublet or a triplet in the f density of states, which is absent in SmB_6, must be explained by the different crystallographic structure of both materials. SmB_6 has the bcc CsCl structure where boron octahedra replace the Cl ions, and SmS has the fcc NaCl structure. In these two structures the d bands which form the lowest conduction band are inverted: In SmB_6 the e_g band is lowest, whereas in SmS the t_{2g} band is lowest. Band-structure calculations for the borides exist only for LaB_6, but with regard to the symmetry of the conduction band no change is expected for SmB_6. The lowest point of the d conduction band is at the X point of the Brillouin zone and the band extending from Γ to X has Δ_2 symmetry. In SmS the minimum of the d conduction band is also at the X point, but it has Δ_2' symmetry.[35–37] Thus in SmB_6 and in SmS the lowest d bands are nondegenerate but they

have opposite parity. Consequently we cannot expect effects due to a lifting of degeneracies of d bands on hybridization with f states.

The f states in SmB_6 and IV SmS are the same and originate from $Sm^{2+}(^7F_0)\Gamma^+$ states and $Sm^{3+}(^6H_{5/2})$ states. The latter split in a cubic crystal field into a lower doublet Γ_7^- and a higher fourfold-degenerate Γ_8^- state. The separation between these states is estimated to be between 4 and 10 meV.[38–41] The operators removing an electron from a Sm^{2+} to create a Sm^{3+} have site symmetry $\Gamma_1^+ \times \Gamma_7^- = \Gamma_7^-$ and $\Gamma_1^+ \times \Gamma_8^- = \Gamma_8^-$.[38] Thus the Γ_7^- and the Γ_8^- f states are those to hybridize with the d bands in the Γ–X direction, where the lower Γ_7^- has Δ_7 symmetry. In a fully relativistic description the d bands also have Δ_7 symmetry, but in SmB_6 the f and d bands have the same parity, whereas in IV SmS they have opposite parity. As a consequence a gap opens up in SmB_6 over the entire Brillouin zone, whereas in IV SmS one has only a pseudogap because the bands cannot hybridize at Γ or X. On the other hand, the possibility exists that the states in the gap are localized so that one has a mobility gap. Proposals in this direction have been made by Kasuya *et al.*,[42] suggesting a Wigner crystallization. Since the f-f transitions in IV SmS have a considerable width (6 meV) because of the strong f-d mixing it is feasible that also the nonhybridizing Γ_8^- can be observed so the splitting in the f-f transitions resembles the crystal-field splitting Γ_7^--Γ_8^-. In SmB_6 with the smaller f-d mixing and the smaller width of the f-f transitions (3 meV) they would fall into the energy range of the f-d transitions where they cannot be observed.

We want to briefly discuss another possibility of the splitting of the f-f transitions, that is electron-phonon coupling. The phonon dispersion of the acoustic branch has been measured by means of inelastic neutron scattering on IV SmS.[43] The well-known depression in the LA (Λ) branch manifests itself in a density-of-states peak at 75 cm^{-1}=9 meV,[44] just as observed[45] and computed[46,47] for the first time for TmSe at 60 cm^{-1}. The energy of the LA phonons is approximately correct and strong polaron effects have been proposed for SmS.[48] Regarding the splitting of the f-f transitions in IV SmS, we thus remain undecided between crystal-field splitting or electron-phonon coupling.

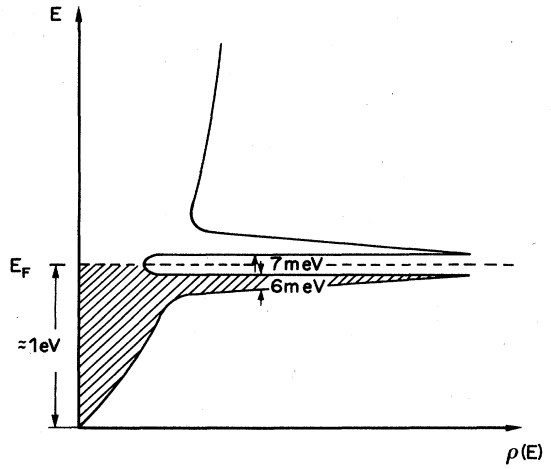

FIG. 6. Electronic structure of IV SmS near E_F.

The band-structure calculation for IV SmS (Ref. 37) permits us to estimate the energy of the f states in the conduction band. The d band will contain about 0.8 electrons lost by the f band and these will fill the d band up to about 1 eV, in excellent agreement with the measurement reported above. We thus are able to give a schematic, but relatively quantitative picture of the density of states of IV SmS in the vicinity of E_F which is depicted in Fig. 6, which excludes the fine structure.

From our measurements of the joint density of states J_{cv} of initial and final f states, we are not able to prove that both states have this giant density of states, despite the fact that the hybridization model makes this very reasonable. In IV SmS we have for the first time the chance to show that the occupied as well as the empty f states are narrow bands with large density of states. The proof is given with the derivation of the effective mass of the thermally excited electrons over the gap at low temperatures, where we found $m^* \leq 360m$ for the f band above E_F, whereas the filled f band below E_F had an effective mass $m^* \approx 150m$. Thus both f bands must be very narrow in agreement with a large density of states.

One last aspect shall be discussed. The apparent gap in IV SmS of about 7 meV is larger than that for SmB_6, 4.4 meV. On the other hand, the resistivity increase between room temperature and about 2 K is more than 5 orders of magnitude for SmB_6,[33] and only about 1 order of magnitude for IV SmS.[27,28] This is exactly what one expects when IV SmS has only a pseudogap. When the density of states at E_F is small compared to the giant density of states of the f peaks, the resistivity may nevertheless appear activated over a certain temperature range as experimentally observed, but for the lowest temperatures metallic conductivity should persist. Indications for this may be found.[28] From the difference of σ_1 in Fig. 4 between minimum (7 meV) and maximum (20 meV), which is proportional to J_{cv}, we conclude that there is about a factor 100 between minimum and maximum J_{cv}. Thus for IV SmS we do not expect a disappearing γ value as for SmB_6. From the γ value[27] of 145 mJ/mol K^2 one computes a density of states at E_F of 830 states per rydberg and cell, which appears much too large (even considering electron-phonon effects) for our J_{cv}'s of 1200 or even 3500 at the density-of-states peak (Table I). We strongly suggest that the specific heat be remeasured on good samples.[27] For comparison the γ value of SmB_6 decreased upon remeasurement from 90 to 6.8 to 2.1 mJ/mol K^2 (Refs. 49, 50, and 51, respectively) with a closing statement that a linear part of the specific heat cannot be established.[51]

CONCLUSION

Despite the difficult experimental situation with producing the high-pressure phase of IV SmS, we have succeeded in measuring the reflectivity over a very large wavelength range and at low temperatures. In the far-infrared region there was a clear distinction between f-f and d-f transitions. A typical value for the oscillator strength for the d-f transitions was 0.368, whereas the f-f transitions had a weak oscillator strength, which was,

however, enhanced by about 3 orders of magnitude due to f-d mixing. The joint density of states of f transitions is about 10—50 times larger than for d transitions. The analysis regarding symmetry and parity of d and f wave functions revealed that IV SmS has only a pseudogap and not a real gap as in SmB_6. The gap was found to be 7 meV, in agreement with a point-contact measurement. Several multiparticle excitations, have been found or are suggested: coupled plasmon excitations, LO-phonon—plasmon (plasmaron) excitations, intra-4f excitations, electron-phonon (polaron) modes and crystal field excitation. The fine structure in the f-f transitions is attributed to one of the latter two excitations. The general result is that also IV SmS corroborates the hybridization model put forward long ago.

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