PHYSICAL REVIEW B VOLUME 23, NUMBER 4 15 FEBRUARY 1981

Dielectric response of mixed-valent TmSe

B. Batlogg*
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule,
CH-8093 Zürich, Switzerland

(Received 27 December 1979)

The optical reflectivity of TmS and of TmSe with varying degrees of valence mixing has been measured in the photon energy range from 30 meV (and partially from 1 meV) up to 12 eV. Intraband absorption below about 2 eV causes the metallic high reflectivity and the metallic lustrous color. The anomalous excitation spectrum of $Tm_{1.0}Se$ at low energy (< 0.5 eV) is attributed to the intermediate valence character of this compound, and is consistent with the model of *d* electrons and holes scattered from partially occupied *f* states at the Fermi level. The most striking result stems from the sum rule and spectral analysis of the collective mode of the conduction-band plasma: those electrons, whose partial *f* character is responsible for the intermediate valence features in TmSe, appear to participate fully in the *d* conduction-band plasma oscillation as if they had no *f* character at all. The one-particle excitations above ~ 2 eV are well explained in terms of transitions from the *p*-valence band and from highly correlated 4*f* states into the double-structured 5*d* conduction band. A comparison with x-ray photoelectron spectra reveals an apparent difference for the value of the effective 4*f* Coulomb correlation energy as determined by the two experiments and points to different final-state interactions.

I. INTRODUCTION

The enormously growing interest in the intermediate-valent rare-earth compounds is based on the challenging problems and features for both theorists and experimentalists. The crucial point is the degeneracy of two electronic configurations, for example, $4f^n$ and $4f^{n-1}5d$, representing two valence states of the rare-earth ions because of the delocalized nature of the 5*d* wave functions. The occupation number of the 4*f* shell is no longer a stable integer.[1-3] The identity of the two constituting configurations may reappear in the experimental results in different ways: The experimental response either consists of a weighted averaged (e.g., lattice constant and Mössbauer isomer shift) or a superposition (e.g., in photoelectron and optical spectra for $h\nu \geqslant 0.1$ eV) of the typical $4f^n$ and $4f^{n-1}5d$ properties. Many results, however, unambiguously point to a qualitatively new ground state in the mixed-valent situation: a lack of magnetic moments at low temperature, giant linear terms in the specific heat, softening of the lattice and anomalous transport properties, just to mention some.

Among all the intermediate-valent (or homogeneously mixed-valent) compounds TmSe is the unique exception insofar as it orders magnetically below 3 K.[4-6] In contrast to intermetallic mixed-valent compounds, but similarly to metallic SmS and SmB_6, in TmSe no other conduction electrons exist than those originally liberated from the 4*f* shell, with the consequence that all the peculiar effects due to the configuration degeneracy can be studied in an unadulturated situation.

Experimentally TmSe has soon been recognized to be tricky in the sense that the chemical composition is hard to control and that the entire physical features sensitively depend upon it.[7-15] After the extended and systematic study of various thermal, magnetic, and transport properties the stoichiometry variation turned out to be a decisive tool to influence the Tm valence.[13-15] From the lattice constant the amount of divalent character has been found to increase from $\sim 0\%$ in $Tm_{0.87}Se$ over 25% in $Tm_{1.0}Se$ to 28% in $Tm_{1.05}Se$, where the subscript indicates the molar ratio of Tm to Se. Within a given sample all Tm ions have been concluded to be in the same configuration and stoichiometric TmSe, therefore, being a *homogeneously* mixed-valent compound with 25% divalent and 75% trivalent character in each Tm ion's ground state.[15] This is supported by recent investigations of the $Tm_{1-x}Y_xSe$ alloy series where even in the single-impurity limit the Tm ions have been found to be of mixed-valent character.[16]

The aim of the present work is to investigate the optical excitation spectrum of an intermediate-valent compound over a wide energy range. Of particular interest are (1) the behavior at low photon energies (meV range), (2) the collective mode of the 5*d* conduction-band plasma, and (3) the interband excitations involving the 4f states. TmSe with varying chemical composition, together with trivalent TmS, is very well suited for this purpose because the valence of the Tm ions in these systems ranges from ~3 to ~2.7, allowing direct comparison between compounds with different degrees of valence mixing.

Reflectivity measurements provide us with the dielectric response function. The depth of probing is given by the inverse absorption coefficient and typically amounts to 10^2 to 10^3 Å, meaning that the optical reflectivity measurements are not surface sensitive.

II. EXPERIMENTAL RESULTS

A first survey over the reflectivity (R) spectra is obtained in Fig. 1. Three distinct regions are obvious: metallic high reflectivity below ~1 eV, a steep edge between ~1 and ~2.5 eV, and above the minimum at ~2.7 eV some less-pronounced structures with a broad maximum of R between 5 and 7 eV. At a glance this spectrum is very suggestive of rare-earth monochalcogenides with the cation in the trivalent state.[17] Because the chalcogen ion accepts just two electrons to fill the valence band derived from its p states, a third electron remains in the conduciton band and is responsible for the metallic character of these compounds. The conduction electrons form a solid-state plasma giving rise to the high reflectivity at the lower photon energy range and the typical edge near the plasma resonance. At higher frequencies, the interband excitations start. The different energy ranges will be discussed separately in the following, because of the different type of information that can be deduced from them.

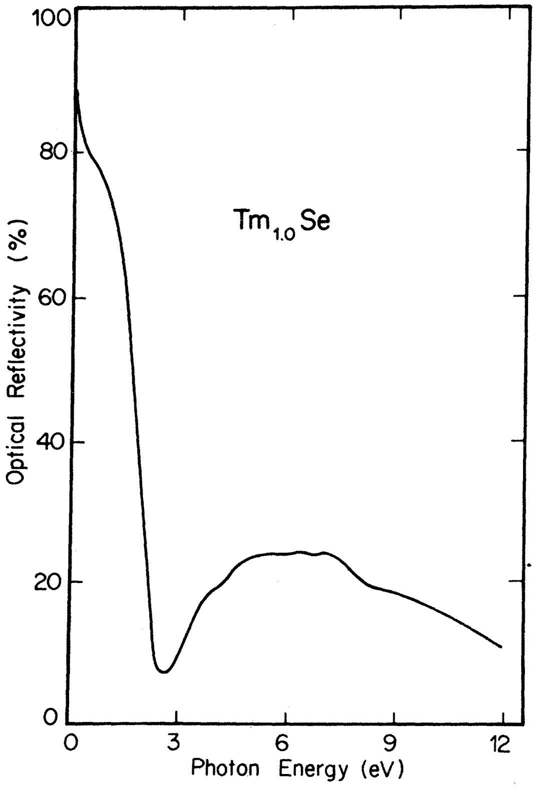

FIG. 1. Optical reflectivity spectrum of Tm$_{1.0}$Se.

III. INTERBAND EXCITATIONS

Although the structure of the spectra is rather rich in the interband region, it would be difficult to explain it unambiguously without any experience with similar substances. Optical and photoelectron spectroscopy on semiconducting and metallic rare-earth monochalcogenides, all crystallizing in the rocksalt structure, led to a universal energy-level scheme of this class of compounds,[18–22] which has been proposed originally for the semiconducting europium chalcogenides.[23] Accordingly, the valence band is derived predominantly from the Se 4p wave functions and the conduction band from the 5d and 6s rare-earth states. Depending on the valency of the rare-earth ion, the crystal is semiconducting if the rare-earth ion supplies just the two electrons to fill up the valence band and it is an ionic metal with one conduction electron per formula unit when the rare-earth ion is trivalent. In addition to valence→conduction-band excitations electron promotion out of the $4f^n$ shell into the empty conduction states is expected in the same energy range. The $n-1$ 4f electrons left behind can also be excited and the energy separations between these multiplets are characteristic and well known for each number n of 4f electrons.[24] This "fingerprintlike" uniqueness of the multiplet spectra makes it easy to determine the occupation number of the 4f shell.

Here we take the opportunity to clarify what kind of excitations involving 4f electrons are to be expected in homogeneously mixed-valent compounds. Since we are dealing here with photon energies in the order of eV and the hybridization energies between 4f and 5d states are two or three orders of magnitude smaller, we are in the so-called "high-frequency" region.[25] This means, that two distinct sets of multiplets appear, corresponding to $4f^n$ and $4f^{n-1}$ initial configurations, as if two species of Tm ions were present in the sample. The spectra then consist of a superposition of integral-valent ion spectra with the intensities given by the amount of divalent and trivalent character in the intermediate-valent ground state. Therefore, it has to be emphasized once again, that both photoelectron and optical (in the eV range) spectra are indeed able to detect a valence mixing, but neither spectroscopy experiment can distinguish between a homogeneous or an inhomogeneous mixing. For that purpose, experiments are needed involving measuring energies comparable to or smaller than both the hybridization energy and the energy difference of the two electronic configurations under discussion.

The $5d$ states, together with the $6s$ ones, form the conduction band but still experience the ligand field. In octahedral surroundings and in the simplifying framework of the point-charge model the energy difference between the atomic triplet t_{2g} state at lower and the doublet e_g at higher energy is proportional to the fourth power of the mean radial extension of the $5d$ wave functions and is inversely proportional to the fifth power of the distance to the surrounding point charges. Also in energy-band calculations the density of the conduction-band states is centered around two maxima.[26–28] And, indeed, the optical spectra of all the Sm, Eu, Gd, and Yb monochalcogenides clearly reveal the double structure assigned to the $5d$ band splitting.[18–20, 29, 30] It is now quite surprising how well these experimentally found splittings Δ can be *parametrized* by the point-charge formula which would never be expected to apply so well for this case. Thus

$$\Delta = d\langle r_d^4\rangle / R^5 \ . \tag{1}$$

Taking the same value for the only parameter d the calculated Δ agrees within better than 10% with the observations. For the rare-earth-ion–chalcogen separation R, it is obvious to take half of the lattice parameter a_0. The appropriate choice, however, of the $5d$ shell radius r_d is less clear. Electron wave functions for the rare earths have been calculated from modified nonrelativistic Hartree-Fock and from relativisitc Dirac-Slater equations and both methods lead to practically identical results.[31–34] For our purpose it is important to note that the maximum of the $5d$ electron charge density and the empirical ionic radius coincide within a few percent. Therefore we replace the $5d$ shell radius by the ionic radius. It is experimentally given, applying a hard-sphere model, by the lattice constant and the chalcogen ion radius. Numerically, this reads

$$\Delta = 1.1 \times 10^4 \frac{(\frac{1}{2}a_0 - r_X)^4}{a_0^5} \ , \tag{2}$$

where Δ is expressed in eV and a_0 and r_X are measured in Å. Optimal overall agreement with the experiments is achieved, putting the chalcogen ion radius $r_X = 1.86$, 1.98 and 2.15 Å for $X = \mathrm{S}$, Se, and Te, respectively. As a manifestation of the growing covalent bonding character on passing from the sulfides to the tellurides the chalcogen ion radii used in (2) deviate very slightly (by less than 3%) from the ones deduced from highly ionic compounds (1.84, 1.98, and 2.21 Å). According to the above parametrization of the experiments (2), the splitting Δ for the Tm chalcogenides can be predicted to be 1.4, ~ 1.0, ~ 1.0, and 1.2 eV for TmS, $\mathrm{Tm_{0.87}Se}$, $\mathrm{Tm_{1.0}Se}$, and $\mathrm{Tm_{1.05}Se}$, respectively.

In the case of homogeneously mixed-valent TmSe the electronic $4f^{13}$ and $4f^{12}5d$ configurations are equivalent in energy. In analogy to the results of the x-ray photoelectron spectroscopy[7] in the optical excitation spectrum we expect $4f^{13} \rightarrow 4f^{12}5d$ and $4f^{12} \rightarrow 4f^{11}5d$ transitions which are separated by ~ 6 eV as a result of $4f$ Coulomb correlations. The former group of multiplets, however, hardly can be observed in the reflectivity spectrum since the conduction-band electron plasma causes a very high

TABLE I. Some physical properties of TmS and $\mathrm{Tm}_x\mathrm{Se}$.

	TmS	$\mathrm{Tm_{0.87}}$	$\mathrm{Tm_{1.0}Se}$	$\mathrm{Tm_{1.05}Se}$
Lattice constant a_0 (Å)	5.42	5.63	5.69	5.715
Tm valence, deduced from a_0	3.0	3.0	2.75	2.72
Reflectivity minimum (eV) (±0.1 eV)	3.15	2.25	2.6	2.8
Onset of $4f^{12} \rightarrow 4f^{11}5d$ excitation (eV) (±0.1)	5.5	5.4	5.4	5.2
Plasmon energy $\hbar\omega_p$ (eV)	5.3	3.6	4.35	4.5
Effective optical mass m^*/m_e	1.3	1.65	1.65	1.65
Electron density N_e(expt) from ω_p (10^{22} cm^{-3}) (±0.1)	2.6	1.53	2.05	2.3
N_e(theor.) with Tm valence from a_0 (10^{22} cm^{-3})	2.5	1.5	1.5	1.65
N_e(theor.) assuming 1 e per Tm (10^{22} cm^{-3})	2.5	1.5	2.05	2.3

reflectivity below ~2.5 eV and therefore masks these rather weak interband-type excitations. The separation in energy between the $4f^{11}$ final states is given by those of trivalent Er, having also 11 electrons in the $4f$ shell, but in order to account for the additional nuclear charge in Tm, the energy scale is expanded by 10%.[35] Considering also the splitting of the $5d$ states by the ligand field into two subgroups, we expect all $4f^{12} \rightarrow 4f^{11}5d$ transitions to occur twice.

A whole set of optical excitations with fixed relative energies is now predicted and ready to be compared with the experiments in Figs. 2(a)–2(c). Solid and broken lines correspond to final states with the excited d electron being either in the lower or higher part of the $5d$ band. The only free parameter is a shift on the absolute energy scale. A fair overall agreement is obtained choosing the minimum $4f^{12} \rightarrow 4f^{11}5d$ excitation energy as given in Table I. For the sake of comparison and completeness the reflectivity spectrum of the nonmixed-valent TmS is shown in Fig. 2(d) and the agreement between predictions and measurements is as satisfactory as for the Tm_xSe spectra. Besides these $4f \rightarrow 5d$ transitions, also excitations from the p-like bonding valence band into the conduction band occur and actually give rise to the rather steep increase of the reflectivity above the minimum which is in the different compounds located between 2 and 3 eV. Any determination of the valence bandwidth from such a spectrum is ambiguous because it would reveal only a lower limit. From photoelectron spectroscopy the width of the p valence band has been deduced to be about 8 eV in TmSe[36] and 6 eV in TmTe.[37] But comparing other experimental findings on both semiconducting and metallic rare-earth monochalcogenides[38,39] and considering the universality of the band structure of all NaCl-structure compounds[40] a valence bandwidth of 5.5, 5, and 4 eV is expected, with about 1-eV uncertainty, for TmS, TmSe, and TmTe, respectively. The discrepancy of more than 50% is surprisingly high and needs further clarifications, since there is no reason known why the valence bands just in the Tm chalcogenides should be extraordinarily wide.

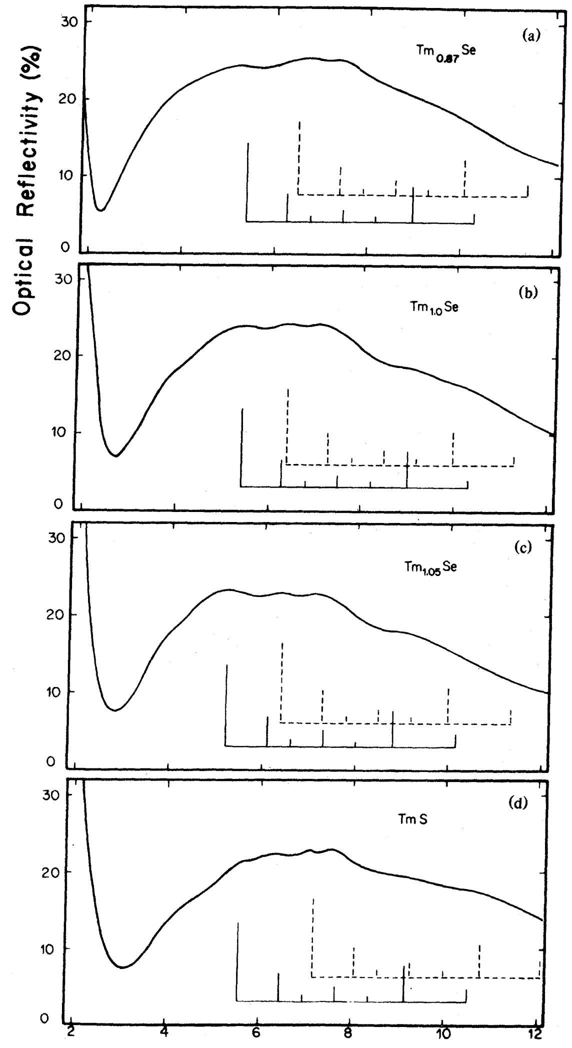

FIG. 2. Part of the optical reflectivity spectrum of Tm_xSe ($x = 0.87$, 1.0, and 1.05) and TmS. The vertical bars indicate the calculated position and strengths of final-state multiplets after $4f^{12}$-$4f^{11}5d$ excitations. (Intensities should be compared only within each subgroup.) Full and broken lines correspond to final states with the $5d$ electron in either the energetically lower or higher part of the conduction band.

The minimum energy necessary to promote an electron from the valence into the conduction band is given by the energy difference between the top of the valence band and the lowest unoccupied conduction states. Variation of the chemical composition of Tm_xSe is reflected not only in the degree of valence mixing but also in the density of the conduction-band electrons. Similar effects occur also in GdS and GdSe with varying stoichiometry.[17] As a consequence of the different filling heights of the conduction band the $p \rightarrow d$ transitions start in $Tm_{0.87}Se$ by ~0.4 and ~0.5 eV lower in energy than in $Tm_{1.0}Se$ and $Tm_{1.05}Se$, respectively. In TmS, however, it is the position of the p band that shifts the p-d onset by +0.7 eV relative to TmSe.

IV. CONDUCTION-BAND PLASMA

The predominant structure of the TmS and TmSe reflectivity spectra is the edge at 2 eV. This sudden drop is characteristic for the metallic rare-earth chalcogenides and is due to a plasma oscillation interfering with interband excitations. This plasma oscillation mode is not directly related to the "free $5d$ electron" behavior. Its resonance character becomes obvious in the energy loss of electrons shot through the material. Although the energy-loss function is closely related to the system's response to longitudinal perturbations, its wave-vector integral value can be calculated from the optically determined transverse zero-wave vector dielectric function

$$\epsilon(\omega,q=0)=\epsilon_1+i\epsilon_2 \ .$$

From the measured reflectivity spectrum $\epsilon(\omega)$ has been evaluated with the help of the Kramers-Kronig relation[41] which connects the real and imaginary part of a linear and casual response function. The imaginary part of the energy-loss function is then obtained as $-\mathrm{Im}(\epsilon^{-1})$ and is shown in Fig. 3. The energy of the conduction electron plasma resonance in the presence of the interband ($f\rightarrow d$, $p\rightarrow d$) excitations is given by $\epsilon_1(\omega)=0$ and the peak maxima in Fig. 3 are shifted only very little from this energy (by $-\sim 0.05$ eV) as a result of damping effects. In the most simplified model to describe the free-electron behavior, the Drude model, only one frequency-independent scattering parameter is used to describe both the collective-mode damping and the zero-frequency electrical conductivity. This assumption leads to a close relationship between these two experimentally accessible quantities, which, however, is not fulfilled in the metallic rare-earth monochalcogenides. But there exists the general trend in the experimental data that the energy-loss peak is the wider the higher in energy it occurs. That is exactly what one expects from a plasma excitation in the presence of interband transitions. Whereas the collective mode of a translationally invariant gas of electrons suffers no damping in the long-wavelength limit ($q=0$), its behavior is markedly altered in the periodic crystal potential. If then the plasma resonance lies below the onset of the interband transitions, their pure real dielectric constant shields the electronic interactions and causes only a reduction of the resonance energy. If, however, the plasma mode and the interband excitations coincide in energy the collective mode is not only shifted in its energy but is also damped additionally due to decay into single-particle excitations. Accordingly, the plasma resonance width and the strength of the interband absorption are expected to be correlated.

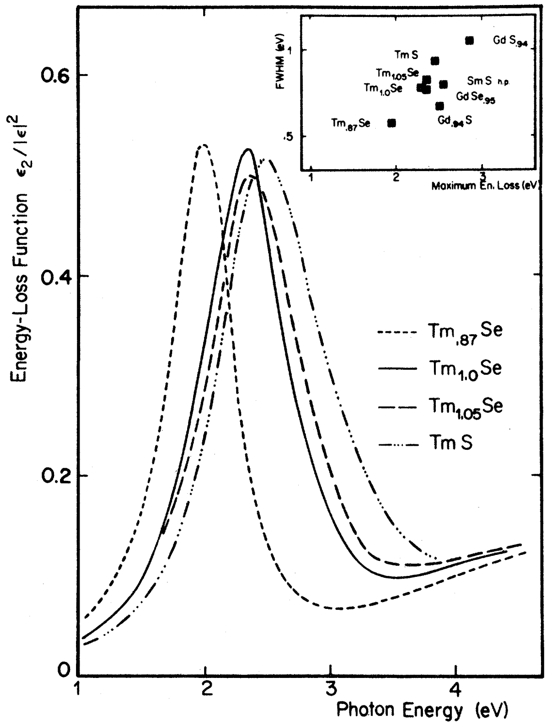

FIG. 3. Imaginary part of the energy-loss function as deduced from optical data, demonstrating the resonance character of the coupled plasma-interband excitation. The insert correlates the energetic position of the maximum with the width for comparable metallic rare-earth compounds, and indicates the decay of plasmons via one-particle interband excitations.

As shown in the insert of Fig. 3, this plasmon decay channel exists at least in the Gd and Tm sulfides and selenides since in these compounds the interband absorption steadily increases in the energy range under consideration.

It would be of basic interest to know the plasma resonance frequency ω_p in *absence* of interband excitations because it carries the important information about the electron gas density and the electron's effective mass. In a metal ω_p is generally given by the integral of the electron velocity over the Fermi surface. In the case of a spheric Fermi surface it reduces to the well-known formula

$$\omega_p=(Ne^2 4\pi)/m^* \ ,$$

where N and m^* denote the electron density and effective mass, respectively. There is some justification for treating the conduction electrons in the metallic rare-earth monochalcogenides to a good approximation as quasifree electrons with an effective mass m^*. Band-structure calculations for the Eu and Sm monochalcogenides[26-28] agree in showing a parabolic minimum of the conduction band, about 1.5 to 2 eV deep and located at the X point in the Brillouin zone. One can estimate that the filling of the conduction band with one electron per cation results in an occupation of only the parabolic part, since photoelectron spectra indicate the conduction band to be filled up to ~ 1.5 eV.[39]

In the optical experiment we measure the response of a coupled system of interband and intraband excitations. Without any further information it would not be possible to make a separation between both kinds of excitations but the deep reflectivity minimum (Figs. 1 and 2) allows us to perform the decomposition in the present case. The minimum comes about because the quasifree electrons at lower and the interband transitions at higher energies are only weakly absorbing in the overlapping energy region. The practical decoupling procedures are based on the additivity of the dielectric functions.

Using the decomposition method successfully applied in Ref. 17, the plasma frequencies ω_p of the quasifree-electron system alone have been calculated and are given in Table I. The next step is to derive the electron density N provided the effective mass m^* is known. In the detailed study of LaS, GdS, and GdSe exactly the same decoupling method has been applied and together with the carrier density as known from Hall-effect data the effective mass m^* in (3) has been determined to 1.3 and 1.65 times the free-electron mass m_e for the sulfides and selenides, respectively.[17] The replacement of Gd by Tm in these compounds causes a lattice contraction of only less than 2% and the band structure is expected to change only very little. Consequently, the same effective mass m^* as for the Gd compounds has been taken for the Tm compounds. The electron densities determined this way experimentally are listed in Table I and will now be compared with expected ones.

The main question to be answered is whether in mixed-valent TmSe the number of electrons participating in the conduction-band plasma oscillation is simply *one per cation* or whether it is given by the *amount of trivalent character* in the mixed-valent ground state. The theoretical density can be calculated starting with the lattice constant and considering the actual occupation number of the cation sites, which is experimentally known by the density of the material and its chemical composition.[42,43] Another correction is necessary because of the variation of the Tm to Se ratio. Since two electrons per Se are needed to fill up the p valence band, in Tm-deficient samples two electrons per missing Tm are drawn away from the conduction band reducing the number of conduction electrons per present Tm. The reverse is expected to occur in the Se-deficient samples ($x > 1$). Taking into account these corrections and *postulating* that the number of collective electrons coming from the Tm ions is given by the Tm valency as deduced from the lattice constant (Table I) the theoretically expected conduction-band plasma density can be calculated and is given in Table I. A comparison with the experimental values reveals an excellent agreement for TmS and $Tm_{0.87}Se$, the two compounds with essentially trivalent Tm ions. Although the few assumptions made above are based on analogy to very similar substances and are reasonable for themselves, they now appear to be justified again.

In the mixed-valent counterparts, however, the experimental electron densities are up to 30% higher than the expected ones. These significant differences are immediately removed if, irrespective of the valence information from the lattice constant or any other valence-sensitive experiment, a valence of +3 is used to calculate the densities. The new modified theoretical densities now are in best accordance with the experiments. This is a striking result and needs a detailed analysis of the method leading to it.

One might argue that the zero crossing energy of ϵ_1 used to calculate the plasma density is not only determined by Drude-type excitations, but also by other low-energy excitations and as those of f electrons at E_F into the conduction band ($f \rightarrow d$). This important point will be illuminated now from two different directions taking $Tm_{1.0}Se$ as an example.

(1) If the conduction-band plasma density were determined by the degree of trivalency the plasma energy would be renormalized accordingly from 4.25 eV to ~ 3.6 eV. In order to observe finally a zero crossing of ϵ_1 again at 4.25 eV the "f-d" transitions under discussion would have to contribute ~ -1 to ϵ_1 at 4 eV. But as known from all semiconducting rare-earth (RE) monochalcogenides, the $f \rightarrow d$ excitations never give rise to a negative ϵ_1 and therefore cannot push the ϵ_1 zero crossing to higher energies. Even an attempt to ignore all known spectral details of the $f \rightarrow d$ transitions and to model them by a resonator with adjustable center frequency and damping is found to fail: Whenever ϵ_1 is negative of order 1 in the eV range, the corresponding value of ϵ_2 ($\sim \sigma_1$) vastly exceeds the experimental upper limits shown in Fig. 4.

(2) The most fundamental argument, however, is based on the sum rule. One version of it counts the number of electrons (n_{eff}) taking part in optical excitations up to a given energy by integration over the real part of the conductivity $\sigma_1(\omega)$. Again we assume that the integer-valent compounds provide us with reliable reference spectra.

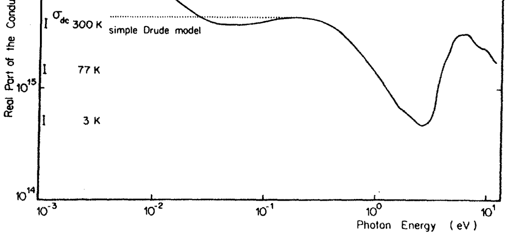

FIG. 4. Real part of the frequency-dependent conductivity. The dotted line indicates a simple Drude behavior. The dc values of σ (taken from a four-probe measurement, Ref. 13) are also given for various temperatures.

In a typical RE chalcogenide with the RE in the trivalent state, like GdSe or TmS, $n_{\mathrm{eff}}(\omega)$ up to ~ 3 eV is dominated by the intraconduction-band absorption. At the energy of the plasma resonance, n_{eff} reaches values between 0.8 and 0.9 electrons per formula unit just as expected from the one electron in the conduction band. (To count the whole oscillator strength and to obtain $n_{\mathrm{eff}}=1$ one has to integrate beyond the plasma resonance.) In a typical semiconductor, on the other hand, like EuO or TmTe, only the $f \rightarrow d$ excitations contribute to n_{eff} below the onset of the $p \rightarrow d$ transitions. The exact value of n_{eff} in this energy range depends, but not sensitively, on details of the $4f$ final-state multiplets. From EuO and TmTe data,[18,37] an upper limit of ~ 0.15 electrons per formula unit at 2 eV can be deduced. (Such a low value is reasonable because the $f \rightarrow d$ transitions are spread over a wide energy range, ~ 10 eV.) Considering the dielectric response of mixed-valent TmSe as being a weighted superposition of the known di- and trivalent spectra, the sum rule predicts n_{eff} at ~ 2.5 eV to be $(1-c)(0.85)+c(0.15)$ where c stands for the degree of divalency. Taking c from the lattice constant (or the effective moment, respectively) this results in an n_{eff} of ~ 0.68 (or 0.57, respectively) for TmSe. The experimental value of 0.86 ± 0.05 is not only significantly higher than expected from the superposition model, but strikingly the same as in TmS (see Fig. 5).

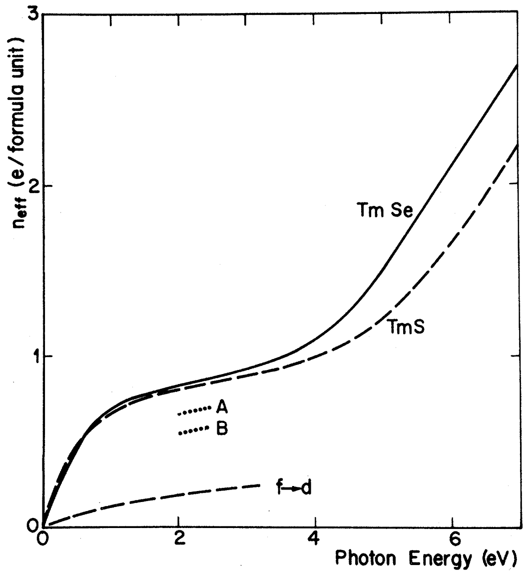

FIG. 5. Numbers of electrons per formula unit that can be excited optically up to a given energy. The curves for TmS and TmSe are experimental data. The contribution of $f \rightarrow d$ transitions is estimated from data on EuO and TmTe (Refs. 18 and 37). If the dielectric response of mixed-valent TmSe was weighted superposition of di- and trivalent spectra, n_{eff} would lie between A and B.

It is therefore from both the spectral dependence of ϵ and the distribution of oscillator strength that we are led to interpret the zero crossing of ϵ_1 in the eV range as determined essentially by a Drude-type of dielectric response involving *close to one electron* per formula unit. This agrees with the numerical analysis of ω_p presented above. But more importantly such a result cannot be anticipated from traditional understandings of the mixed-valent state and its dielectric response. It appears as if the "extra electron" which plays the dominant part in forming the mixed-valent ground state $(4f^{12} \rightarrow 4f^{11}5d)$ acts like it had only and fully the same character as the other (d) conduction-band electrons.

At this point, a comparison with two other homogeneously mixed-valent compounds may reveal if TmSe is an exceptional case. In metallic SmS, the analysis of the optical data revealed a density of $5d$ conduction electrons, participating in the plasma resonance, of 0.92 e/Sm and has been found to agree rather well with the Sm valence of 2.85 deduced from the lattice constant.[20] But now being aware of the present results on TmSe, the value of 0.92 might as well be interpreted to be close to 1 and therefore not to be in contradiction to the most recent findings. In the case of the other example, SmB_6, the plasma density has not been evaluated,[44] but a first comparison of its optical reflectivity spectrum with the one of LaB_6 (Ref. 45) leads to the conclusion that the carrier density is within $\sim 10\%$ the same in both compounds. The difference, however, is expected to be very pronounced, since an intermediate valence of 2.6 has been reported for Sm in SmB_6,[46–48] whereas La is integer trivalent in LaB_6. In summary, the "extra" electrons appear to behave anomalously with respect to the conduction-band plasma excitation not only in TmSe, but also in the two very closely related mixed-valent compounds: metallic SmS and SmB_6.

In the above comparison, another mixed-valent compound, CeN, has not been taken into consideration on purpose, since several indications exist for an overlapping of the valence with the conduction band.[49,50] This presence of a third kind of electronic state, in addition to f and d states, creates a totally different possibility of hybridization with a so far undefined influence upon the valence mixing. At least the normal metallic temperature dependence of the electrical resistance,[51] in contrast to the strong increase of ρ at low temperature in TmSe, SmS, and SmB_6, might be caused by the semimetallic character of CeN.

V. LOW-ENERGY EXCITATIONS

As mentioned above, the optical reflectivity of TmSe is metallic high below about 1-eV photon energy, and in usual metals an interpretation in terms of only intraband absorption is appropriate. In the intermediate-valent TmSe, however, it is worthwhile to investigate just the low-energy range because only very little is known about the low-lying excitations of a mixed-valent compound.

In Fig. 6 the reflectivity of a polished $\mathrm{Tm}_{1.0}\mathrm{Se}$ sample is shown on a semilogarithmic scale for photon energies above 1 meV.[52] Polishing the crystal is indispensable since in the absolute measurements of the reflectivity any intensity loss due to surface scattering has to be avoided. The influence of this mechanical treatment has been checked in the eV range and no qualitative changes other than a small shift of the reflectivity minimum at 2.7 eV by less than 0.1 eV could be detected.

For the sake of comparison the dotted line in Fig. 6 represents the reflectivity spectrum of a model "Drude metal" whose parameters are obtained by fitting the behavior close to the edge. The anomalies of TmSe are now obvious: whereas R or TmSe in the 0.1-eV range is lower than of the model metal, it exceeds the dashed curve below ~ 30 meV.

The quantitative discussion will be based on the frequency dependence of the conductivity, whose real part $\sigma_1(\omega)$ equals $[\omega\epsilon_2(\omega)]/4\pi$ and is displayed on a double logarithmic plot in Fig. 4. The uncertainty at the low-frequency limit in Fig. 4 is caused by the different extrapolations of the reflectivity towards zero photon energy, a procedure necessary to perform the Kramers-Kronig analysis.

The minimum of σ_1 at ~ 2.6 eV separates the interband from the intraband excitations. In a well-behaved metal, the conductivity below the minimum would increase towards lower frequency as it does also in TmSe and then tend to level off and would finally reach the dc limit. Apparently, $\sigma_1(\omega)$ of TmSe markedly deviates twice from the simple Drude model: σ_1 is about the same around 0.05 eV but is higher by a factor of 2 in the meV range. Experimentally known also is the dc conductivity (4.3×10^3 $\Omega^{-1}\,\mathrm{cm}^{-1} \triangleq 3.9\times10^{15}\ \mathrm{sec}^{-1}$), determined by a four-probe technique and indicated in Fig. 4. In order to join the dc value, σ_1 therefore has to drop again at still lower frequencies than covered in the present experiment. In addition to the room-temperature behavior of the dielectric response, its variation at lower temperature is of interest, because the dc resistivity continuously increases upon cooling. The interaction between the d and f electrons is presumed to be the reason and its strength is expected to be comparable with the photon energies used in the present work. In Fig. 6 the optical reflectivity is indicated also for $T=77$ K. The following statements based on this 77-K curve are not to be taken quantitatively because of the experimental uncertainty in the intermediate-energy range (0.02 to 0.6 eV) which had to be bridged by a smooth interpolation. The main conclusion, however, is not affected: The reflectivity at 0.02 eV and 77 K is by 7% lower than at 300 K and appreciably smaller than the one of a Drude model. As a consequence also the conductivity σ_1 at that frequency drops below the model behavior and is therefore in agreement with the decrease of the dc conductivity. Obviously the dielectric response of homogeneously mixed-valent TmSe deviates from the Drude model below the 0.1-eV range and it is also worthwhile to note that the anomalous dc behavior is reflected in the dielectric response at such high energies. It has to be noted that these anomalies do not affect the reasoning in the preceding chapter about the plasmon energy, since the total n_{eff} associated with them is less than 2×10^{-2} e/formula unit.

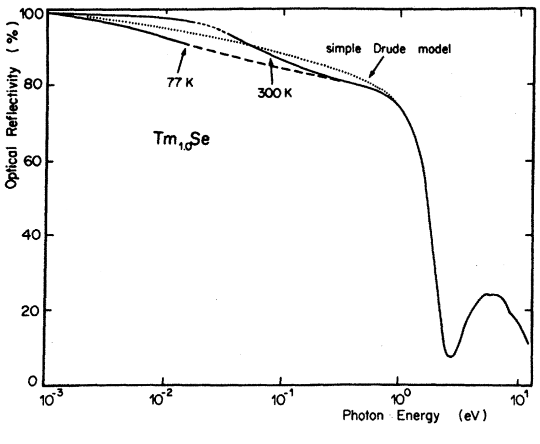

FIG. 6. Optical reflectivity of intermediate-valent $\mathrm{Tm}_{1.0}\mathrm{Se}$. The full curve represents the measurement and the broken lines are interpolations. The dots correspond to a simple Drude behavior for an ordinary metal.

Anomalies in the optical spectrum at low energies have been observed in two other well-established mixed-valent compounds: SmB_6 (Ref. 53) and "metallic" SmS.[54] Some peculiarities in the EuB_6 spectrum have been interpreted with a small degree of valence mixing,[55] but the sample preparation is a delicate problem and according to most recent results Eu now appears to be pure divalent in EuB_6.[56]

The dielectric response spectrum of TmSe will be critically compared with some theoretical work explicitly dealing with intermediate-valent compounds. In a first model Kaplan *et al.*[57] discuss the properties of the Sm chalcogenides based on an "essentially excitonic" picture of most of the $5d$ electrons in the high-pressure ("metallic") phase of SmS. Whereas only ~ 0.1 $5d$ electron per Sm occupy free-electron states, the other remains localized. The optical response will then consist of two ordinary Drude-type intraband contributions corresponding to the heavy $4f$ and to the light $5d$ electrons and an interband term resulting from transitions from the occupied narrow f band. Additional low-energy intra-atomic absorption between ground and excited mixed states are predicted in the range of 0.1 eV. Because the latter are not specified further, they cannot be compared with the experiment and we will concentrate therefore on the $5d$ intraband excitation. In the model, the $5d$ plasma resonance should be much lower in energy than the observed one (4 to 5 eV) since only a fraction of a $5d$ electron is delocalized. To overcome this apparent discrepancy, f to d *inter*band excitations have to be assumed to enhance the $5d$ plasma frequency. This enhancement factor depends upon interband momentum matrix elements and the energy spectrum of the two-band model and should finally give rise to a Drude behavior, but nothing is said about the origin of the corresponding damping term. There is good reason to assume TmSe and metallic SmS to be similar with respect to the band structure and the degree of valence mixing. The "essentially localized $5d$" model in the case of TmSe is faced with the following problem: The stoichiometry variation of TmSe allowed shifting of the amount of divalent character from almost 0 to $\sim 30\%$, furthermore, TmS serves as a nonmixed-valent standard. As discussed in detail in the preceding section, in *all* these compounds the $5d$-electron intraband excitations and their plasmon energies are even quantitatively well explained assuming a completely delocalized $5d$-electron system. It is, on the other hand, an obvious problem to manage the *inter*band enhancement factor is such a way that, irrespective of the valence mixing, the $5d$ *intra*band characteristics would agree with the experiments. In particular, it is not clear how the gradual transition from the nonmixed-valent $Tm_{0.87}Se$ to the mixed-valent $Tm_{1.0}Se$ should be described and why the plasmon damping is comparable in all the compounds studied here. One is therefore left with the two possibilites that either all the parameters in the mode (bandshapes, interband absorption damping, oscillator strength) by accident are such as to reproduce the measurements, which also can be quantitatively interpreted in terms of $5d$ intraband absorption in both mixed- and nonmixed-valent compounds, or that the model just does not apply in the present case.

A second speculation concerning anomalous low-energy excitations is mentioned in the review article by Varma.[2] He points to the possibility of out-of-phase oscillations of the heavy f electrons against the much lighter d electrons, which is called the f-d acoustic mode. The ratio of the Fermi velocities of the two species of electrons determine the dispersion of this mode and its energy at the Brillouin-zone boundary can be estimated to be some 0.1 of an eV. Since it is not yet clarified how it contributes to the zero wave-vector response of the system and whether it is at room temperature Landau damped as a result of the thermal motion of the f electrons, the existence of the f-d acoustic mode is neither confirmed nor precluded by the experiment.

The optical properties of intermediate-valent compounds are treated in a conventional picture by Suzuki *et al.*[55] for $T=0$ and neglecting any new phenomena brought about by the valence mixing, such as f-d interaction, for instance. Accordingly only intra d $f\rightarrow d$, and $d\rightarrow f$ transitions are of importance at low energies. Whereas the former are described by a simple Drude expression, the latter are determined by the position and the shape of the $4f$ density of states. In order to get some agreement with the experiments, the $4f$ states had to be assumed to be 0.4 to 0.5 eV wide in SmS and SmB_6, which is at least one order of magnitude wider than commonly inferred from the experiments and calculations.[2] Because of the lack of any f-d interaction it is not possible to transfer this model to the present case of a strongly temperature-dependent low-energy absorption.

Last, but not least, the most detailed treatment of this subject by Allen *et al.*[44] has to be discussed. The f-d mixing is explicitly included in this description and causes the $4f$ levels to acquire a width Δ. They are located at the Fermi energy and because of their partial occupation (=intermediate-valent situation) the $4f$ sites act for $kT \gg \Delta$ as noncorrelated resonant scattering centers for both d electrons and holes at the Fermi surface. The results for the dielectric function can be cast into a Drude-like expression but with a frequency- and temperature-dependent lifetime τ for the d electrons:

$$\epsilon(\omega,T)=1-\omega_p^2/\{\omega[\omega+i\tau(\omega,T)]\} \ .$$

The explicit dependence of the complex τ upon ω and T is not possible to be given analytically, but has to be calculated numerically. The main features are the following: For photon energies well above the f-d matrix element (typically ~ 0.1 eV) the dielectric response at all temperatures is that of ordinary d-electron intraband excitations. But it is markedly altered at lower energy: At sufficiently high temperatures ($kT \gg \Delta$) a plasmonlike response is expected because electrons are thermally excited well above the states where they suffer strong scattering. At low temperatures, $\sigma(\omega)$ decreases towards low frequency, dropping below the Drude behavior as extrapolated from the unaffected d-intraband excitation range (at eV photon energy), and therefore reflects also the dc behavior in the right way. In the framework of the f-d scattering theory it is possible to interpret qualitatively the optical reflectivity of (intermediate-valent) TmSe. It is not only the frequency dependence over the most extended range so far investigated in intermediate-valent compounds, but also the low-temperature behavior that favors the description of the dielectric properties in terms of $5d$ electrons and holes strongly scattered at the partially occupied $4f$ states at the Fermi level.

VI. ENERGY-LEVEL DIAGRAM AND DISCUSSION

All the information extracted from the optical spectra allows one to compose a rough energy-level diagram. The meaning of such a representation including both correlated multielectron and single-electron states has been discussed already (see Ref. 20, e.g.).

In Fig. 7, the energy-level schemes of TmS and Tm_xSe are shown with the Fermi level as the common reference point. The top of the valence band is given by the onset of the $p \rightarrow d$ adsorption and its width, although not being determined in the present experiment, is indicated with 4–5 eV. On reasons discussed above, the conduction band is represented with two maxima. We have adjusted the Fermi energy in Fig. 7 according to the number of electrons experimentally found participating in the plasma oscillation. Taking a height of ~ 1.5 eV for one electon per cation as is known from photoemission spectra, even the relative variations in the Tm_xSe series lead to very meaningful results, namely, a rather constant gap betwen the bottom of the conduction and the top of the valence band (~ 1.2 eV). The localized $4f^n$ states might be added to these schemes in locating them at an energy below E_F that is the minimum photon energy to promote one electron out of the $4f$ shell into a conduction-band state. In the framework of this convention, the $4f^{12}$ states of pure trivalent TmS lie 5.6 eV below the Fermi level.

For the intermediate-valent $\text{Tm}_{1.0}\text{Se}$ and $\text{Tm}_{1.05}\text{Se}$ the energy-level schemes need further explanation. The peak at E_F only symbolizes the high density of states due to the degeneracy in the energy of the $4f^{13}$ and $4f^{12}5d$ configurations, but not the low-lying excitations of the intermediate-valent ground state. As discussed above, its excited states at high energy (eV) consist of ordinary $4f^{12} \rightarrow 4f^{11}5d$ and $4f^{13} \rightarrow 4f^{12}5d$ one-electron transitions with an intensity factor corresponding to the amount of divalent and trivalent character in the ground state. The broken lines in the level scheme indicate the photon energy, with respect to E_F at which the first $4f^{12} \rightarrow 4f^{11}5d$-type excitations of the mixed-valent system occur, and it equals the optically determined effective $4f$ Coulomb correlation energy U_{eff} (5.3 ± 0.2 eV). In x-ray photoelectron spectra U_{eff} have been found to be 6.6 eV.[7] The difference of 1.2 eV gives evidence that final-state interactions cannot be neglected in either experiment. It would be worthwhile to study further the role of screening and excitonic interaction in these metallic rare-earth compounds.

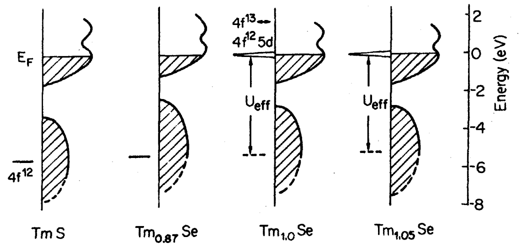

FIG. 7. Energy-level schemes consistent with the optical data.

VII. CONCLUDING REMARKS

The dielectric response of homogeneously mixed-valent TmSe for photon energies between 0.1 and 12 eV qualitatively resembles the trivalent rare-earth chalcogenides. It is dominated by conduction electron absorption below some 2 eV and by interband ($p \rightarrow d$, $f \rightarrow d$) excitations above. The latter group of transitions agree fairly well in energy with predictions based on an empirical rule for related isostructural rare-earth compounds. It is worth noting that the minimum energy required to induce optically the $4f^{12} \rightarrow 4f^{11}5d$ transition is by 1.2 eV smaller than the comparable energy in the x-ray photoelectron spectra. Consequently, the values of the effective $4f$ Coulomb correlation energy as deduced from these two experiments are also different, and this is a manifestation of non-negligible final-state interactions such as screening and excitonic binding.

Below ~0.1 eV strong frequency- and temperature-dependent deviations from a simple Drude metallic behavior characterize the dielectric response. It is concluded that they are typical for the mixed-valent situation and are caused by the presence of $4f$ states at the Fermi level. The results are consistently explained in a framework of d electrons and holes resonantly scattered from uncorrelated f states at the Fermi surface.

A most important new aspect results from the analysis of the collective mode of the conduction-band plasma in intermediate-valent TmSe. The "extra" electron, that makes the difference between the pure ionic configurations $4f^{13}$ and $4f^{12}5d$, apparently fully participates in the plasma oscillation as it would have only delocalized $5d$ character. But simultaneously it is just its partially localized $4f$ character that has been thought to give rise to all the typical intermediate-valence features like, e.g., the intermediate lattice constant, the two sets of $4f$ final states in XPS spectra, and the intermediate effective magnetic moment.

The answer to this obvious contradiction might be expected from a microscopic theory treating both the ground-state properties and the excitation spectrum of a homogeneously mixed-valent system like TmSe.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor Dr. P. Wachter for continuous interest, advice, and generous support of this investigation. He is also very grateful to PD Dr. E. Kaldis for growing and chemically characterizing the single crystals, to Dr. P. Brüesch from the Brown Bovery Research Center in Baden for the far-infrared reflectivity measurements, and to all colleagues and friends of the Solid State Physics Laboratory, Eidgenössiche Technische Hochschule, for valuable discussions, in particular to Dr. H. R. Ott, Dr. A. Schlegel, Dr. J. Schoenes, Dr. A. Treindl, Dr. J. Vitins, and Dr. H. von Känel. The technical assistance of Mr. K. Mattenberger, Mr. H. J. Müller, Mr. H. P. Staub, and Mr. B. Näf, and the financial support of the Schweizerischer Nationalfonds are gratefully acknowledged.

---

[*] Present address: Bell Laboratories, Murray Hill, N.J. 07974.

[1] For an introductory review this and the following two references are recommended to the reader: *Proceedings of the International Conference on "Valence Instabilites and Related Narrow Band Phenomena,"* edited by R. D. Parks, (Plenum, New York, 1977).

[2] C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).

[3] J. H. Jefferson and K. W. H. Stevens, J. Phys. C 11, 3919 (1978).

[4] H. R. Ott, K. Andres, and E. Bucher, in *Magnetism and Magnetic Materials—1974 (San Francisco),* edited by C. O. Graham, G. H. Lander, and J. J. Rhyne AIP Conf. Proc. No. 24 (AIP, New York, 1974), p. 40

[5] B. B. Triplett, N. S. Dixon, P. Boolchand, S. S. Hanna, and E. Bucher, J. Phys. (Paris) Colloq. 35, C6-653 (1974).

[6] H. Bjerrum-Møller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. 39, 1021 (1977).

[7] M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. 32, 885 (1974).

[8] B. Batlogg, A. Schlegel, and P. Wachter, Physica 86-88B, 229 (1977).

[9] A. Berger, E. Bucher, P. Haen, F. Holtzberg, F. Lapierre, T. Penney and R. Tournier, in Ref. 1, p. 491ff.

[10] W. M. Walsh, Jr., K. Andres, L. W. Rupp, Jr., and L. D. Longinotti, in Ref. 1, p. 499ff.

[11] H. R. Ott, B. Lüthi, and P. S. Wang, in Ref. 1, p. 289ff.

[12] P. Haen, F. Holtzberg, F. Lapierre, T. Penney, and R. Tournier, in Ref. 1, p. 495ff.

[13] B. Batlogg, E. Kaldis, and H. R. Ott, Phys. Lett. 62A, 270 (1977).

[14] F. Holtzberg, T. Penney, and R. Tournier, J. Phys. (Paris) Colloq. 40, C5-314 (1979).

[15] B. Batlogg, H. R. Ott, E. Kaldis, W. Thöni, and P. Wachter, Phys. Rev. B 19, 247 (1979).

[16] A. Berger, P. Haen, F. Holtzberg, F. Lapierre, J. M. Mignot, T. Penney, O. Peña, and R. Tournier, J. Phys. (Paris) Colloq. 40, C5-364 (1979).

[17] W. Beckenbaugh, J. Evers, G. Güntherodt, E. Kaldis, and P. Wachter, J. Chem. Solids 36, 239 (1975).

[18] G. Güntherodt, Phys. Condens. Matter 18, 37 (1974).

[19] R. Suryanarayanan, J. Ferre, and B. Briat, Phys. Rev. B 9, 554 (1974).

[20] B. Batlogg, E. Kaldis, A. Schlegel, and P. Wachter, Phys. Rev. B 14, 5503 (1976).

[21] E. Kaldis, A. Schlegel, P. Wachter, and Ch. Zürcher, J. Magn. Magn. Mater. 3, 1 (1976).

[22] M. Campagna, G. K. Wertheim, and E. Bucher, in *Structure and Bonding,* edited by J. Dunitz *et al.* (Springer, Berlin, 1976), Vol. 30

[23] S. Methfessel, Z. Angew. Phys. 18, 414 (1965).

[24] *Spectra and Energy Levels of Rare Earth Ions in Crystals,* edited by G. H. Dieke (Interscience, New York, 1968).

[25] C. E. T. Goncalves da Silva and L. M. Falicov, Phys. Rev. B 13, 3948 (1976).

[26] S. J. Cho, Phys Rev. B 1, 4589 (1970).

[27] H. L. Davis, in Proceedings of the 9th Rare Earth Conference, 1971, Blacksburg, Virginia (unpublished).

[28] K. Lendi, Phys. Condens. Matter 17, 215 (1974).

[29] G. Güntherodt, in *Festkorperprobleme (Advances in Solid State Physics),* edited by J. Treusch (Vieweg, Braunschweig, 1976), Vol. XVI, p. 95.

[30] P. Wachter, Phys. Rep. 44, 159 (1978).

[31] F. Hermann and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, New Jersey, 1963).

[32] A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[33] O. J. Souers, J. Phys. Chem. Solids 28, 1073 (1967).

[34] J. T. Waber and Don T. Cramer, J. Chem. Phys. 42, 4116 (1965).

[35] P. Anthony Cox, in *Structure and Bonding,* edited by J. D. Dunitz *et al.* (Springer, Berlin, 1975), Vol. 24.

[36] M. Campagna, J. E. Rowe, S. B. Christman, and E. Bucher, Solid State Commun. 25, 249 (1978).

[37] R. Suryanarayanan, G. Güntherodt, J. L. Freeouf, and F. Holtzberg, Phys. Rev. B 11, 4215 (1975).

[38] P. Munz, Helv. Phys. Acta 49, 281 (1976).

[39] D. E. Eastman, F. Holtzberg, J. Freeouf, and M. Erbudak, in *Physics and the Energy Problem—1973* (APS, Chicago), edited by M. D. Fiske and W. W. Havens, AIP Conf. Proc. No. 19 (AIP, New York, 1973), p. 1030.

[40] S. T. Pantelides, Phys. Rev. B 11, 5082 (1975).

[41] The author is very grateful to Dr. A. Schlegel from the same laboratory for the help with the Kramers-Kronig computer program.

[42] B. Fritzler, Diplome thesis (Laboratorium für Festkörperphysik ETH, April 1978) (unpublished).

[43] E. Kaldis, B. Fritzler, and W. Peteler, Z. Naturforschung. (in press).

[44] J. W. Allen, Richard M. Martin, B. Batlogg, and P. Wachter, J. Appl. Phys. 49, 2078 (1978).

[45] E. Kierzek-Pecold, Phys. Status Solidi 33, 523 (1969).

[46] A. Menth, E. Buehler, and T. H. Geballe, Phys. Rev. Lett. 22, 295 (1969).

[47] R. L. Cohen, M. Eibschütz, and K. West, Phys. Rev. Lett. 24, 383 (1970).

[48] J.-N. Chazalviel, M. Campagna, G. K. Wertheim, and P. H. Schmidt, Phys. Rev. B 14, 4586 (1976).

[49] J. Dananan, C. de Norion, and R. Lallement, Solid State Commun. 7, 1103 (1969).

[50] A. Schlegel, E. Kaldis, P. Wachter, and Ch. Zürcher, Phys. Lett. 66A, 125 (1978).

[51] B. Batlogg, P. Wachter, and Ch. Zürcher (unpublished).

[52] The author is very grateful to Dr. P. Brüesch from the Brown Bovery Research Center, Baden, for the measurements in the far-infrared spectral range.

[53] J. W. Allen, in Ref. 1, p. 553.

[54] B. Batlogg and P. Wachter, in Ref. 1, p. 537.

[55] T. Suzuki, Y. Isikawa, T. Tanaka, K. Takegahara, and T. Kasuya, in Extended Abstracts of the U.S.-Japan Seminar on Physical Properties of Rare Earth Magnetic Semiconductors, Sendai, 5–7 October 1977 (unpublished).

[56] T. Kasuya, K. Takegahara, M. Kasaya, I. Isikawa, and T. Fujita, J. Phys. (Paris) Colloq. (in press).

[57] T. A. Kaplan, S. D. Mahanti, and M. Barma, in Ref. 1, p. 153.