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Effects of interconfiguration fluctuations upon the far-infrared and dc-transport properties of the thulium-chalcogenides

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The far-infrared reflectivity and dc resistivity of TmX(X = Te, Se, S) were measured as a function of temperature from 1 K to room temperature; the Hall constant of TmSe was also measured. Most of the properties of TmTe were semiconductorlike with a reststrahlen band at 120 cm^{-1}. However, the low-temperature resistivity could not be fit by a thermal activation model and weak, sample-dependent structure appeared in the reflectivity above the reststrahlen band above 2.5 K. Interconfiguration fluctuations are suggested as the cause. The reflectivities of TmSe and TmS are much more metallic; TmS shows a possible weak reststrahlen band at ~ 190 cm^{-1}. The dc transport properties are not like those of a simple metal in their temperature dependences, but may be explained by Kondo scattering from Tm^{3+} ions in the temperature range studied.

I. INTRODUCTION

The existence of interconfiguration fluctuations (ICF) or nonintegral valence of the Tm ion in the Tm monochalcogenides has been proposed as an explanation of their transport, magnetic, and optical properties.[1-5] A connection between valence and lattice constant of these rocksalt-structure crystals is well established.[1] The series TmTe, TmSe, TmS comprises a "transition" in lattice constant from the value near that expected (from extrapolation of similar compounds) for a divalent compound (TmTe) to the value expected for a trivalent compound (TmS) with an intermediate value for TmSe. The relative values of dc and optical conductivities confirm the addition of a conduction electron. However, careful examination of the temperature dependences of conductivity and reflectivity reveals several anomalous results, for which ICF have been invoked. Recently it was asserted that deviations from perfect stoichiometry and/or other lattice defects can account for all the observed effects.[6] However, a mixed-valence state is essential to a full explanation[7,8] of the temperature and magentic field dependences of the transport properties of TmSe and TmS.

In this paper we present experimental results on the temperature dependence of the far-infrared reflectivity of TmX (X = Te, Se, S) as well as the temperature dependence of the dc conductivity of the same samples of these compounds and data on the Hall effect in TmSe. These are interpreted in the light of available models.

Preliminary results[9] on the spectra of TmTe and TmSe were reported earlier; the present results include corrections which result in agreement with the low-frequency data of Batlogg *et al.*[6] and alter some of our earlier conclusions. The spectrum of TmS is also consistent with their results and shows no anomalous behavior. The resistivity of TmTe and its temperature dependence are sample dependent and quite different from the values reported by Bucher *et al.*[1] We find that ICF remain a possible explanation for effects observed in our samples of TmTe, but these may be due to deviations from perfect stoichiometry. We also note that ICF are consistent with the low-temperature transport properties of TmSe and TmS.

II. EXPERIMENTAL

The reflectivity measurements were made using Fourier-transform spectroscopy for broad-band spectra. A lamellar grating interferometer served as energy analyzer in the range 5–50 cm^{-1}; a Michelson interferometer was used for 40–300 cm^{-1}. Single-crystal samples were mounted in one side of a dual nonresonant cavity system[10] and the spectrum of the radiation leaving this cavity was compared digitally with that from the reference cavity. The detector was a ^{3}He-cooled doped Ge bolometer housed in the same cryostat. Sample temperature could be varied from 1.3–300 K using resistance thermometry and a controlling bridge; accuracy was better than ±0.1 K below 4 K, better than ±0.5 below 20 K, and better than ±1 K over the rest of the range.

The absolute values of reflectivity were checked at room temperature using a CO_2 laser at 10.6 μ(= 943 cm^{-1}) and a molecular laser at several frequencies through the range 6–50 cm^{-1}.

The dc resistivity of the same samples as studied spectroscopically was measured using either Van der Pauw (TmSe and TmS) or conventional (TmTe) geometry. Thermocouples or Ge resistance thermometers were used for temperature measurement; resistance readings were taken as samples warmed and cooled slowly. Temperature accuracy was ±1 K above 60 K, improving to better than ±0.2 K at 1 K. Relative values of resistivity are accurate to better than ±1%; absolute values to ~10% due to deviations from ideal sample geometry. Hall-effect measurements were made in a 50-kOe magnet using the Van der Pauw geometry on the same sample as studied by the other techniques. Temperature was measured and controlled using a thermocouple-controlled heater.

The samples were either cleaved single crystals (TmTe and TmSe) or optically smooth polished polycrystalline slabs (TmS). All were grown[1] at Bell Laboratories by L. Longinotti; TmTe and TmSe were provided through the courtesy of E. Bucher. The lattice constants were measured by conventional x-ray powder techniques to an accuracy of ±0.02 Å.

III. RESULTS

The dc resistivities of the three materials at room temperatures differed greatly as did the form of the corresponding temperature dependences. We shall discuss the three materials separately.

a. TmTe. The room-temperature resistivity of TmTe was low and sample dependent. Two samples were studied in our laboratories. Both were grey-black in color; they had lattice constants $a = 6.29 \pm 0.02$ Å and $a = 6.32 \pm 0.02$ Å. The sample whose lattice constant $a = 6.32$ Å did not cleave well, suggesting significant internal strains. The corresponding values of $\rho(300)$ were 2.3 and 0.10 Ω cm. The temperature dependences are shown in Fig. 1. Also shown are data by Bucher *et al.*[1] on a difference sample with $a = 6.364 \pm .002$ Å and $\rho(300) = 59.7$ Ω cm. All resistivities decrease with increasing temperature, typical of semiconductor behavior. In Fig. 2 we present semilog plots of ρ vs $10^3/T$ for our samples, since an intrinsic semiconductor would be expected to exhibit $\rho(T) \sim \exp(\Delta/2kT)$. Activation energies Δ of 0.30, 0.16, and 0.030 eV are found from the linear fits in the high-temperature regions to the data of Bucher *et al.*[1] and samples, Nos. 1 and 2, respectively.

b. TmSe. The sample of TmSe was a reddish-brown single crystal whose lattice constant was measured to be $a = 5.64 \pm 0.02$ Å. The room-temperature resistivity was found to be 700 ± 70 μΩ cm; the resistivity rises with decreasing temperature, but not as sharply as in the case of TmTe.

The temperature dependence of the resistivity is given in Fig. 3 for our sample along with data previously reported.[1] Our data are in agreement with theirs in that there is no region where ln ρ is pro-

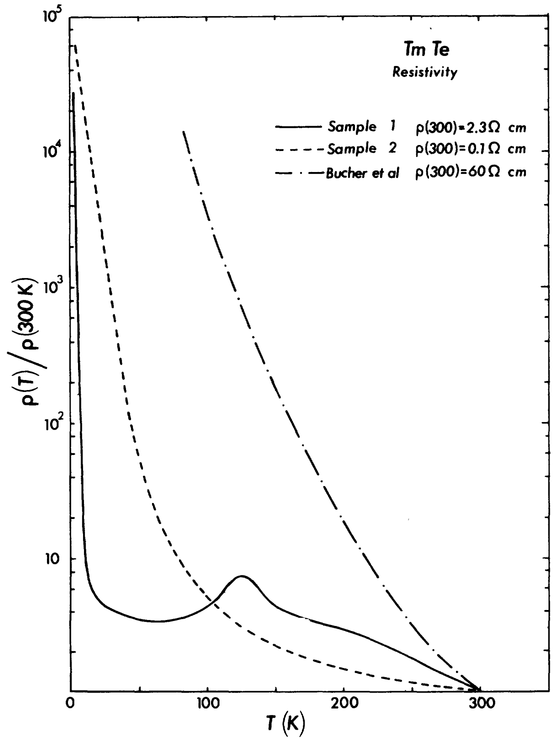

FIG. 1. dc resistivity of three samples of TmTe as a function of T.

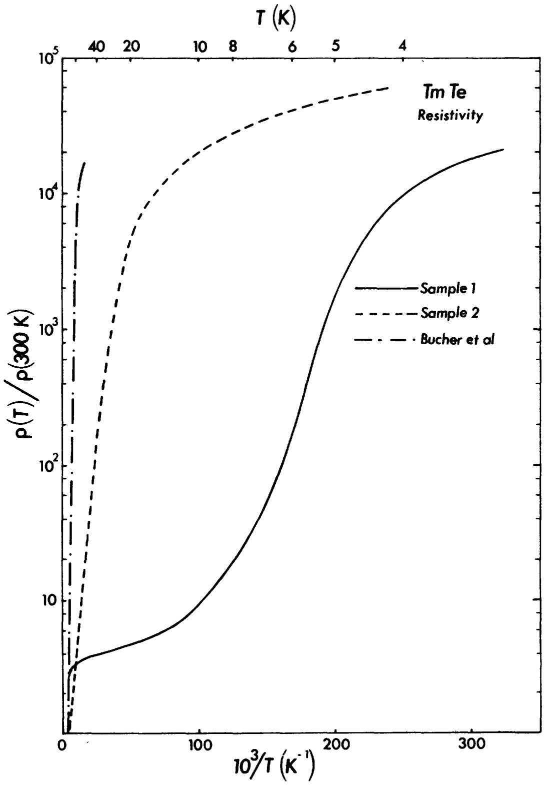

FIG. 2. dc resistivity of three samples of TmTe as a function of T^{-1}.

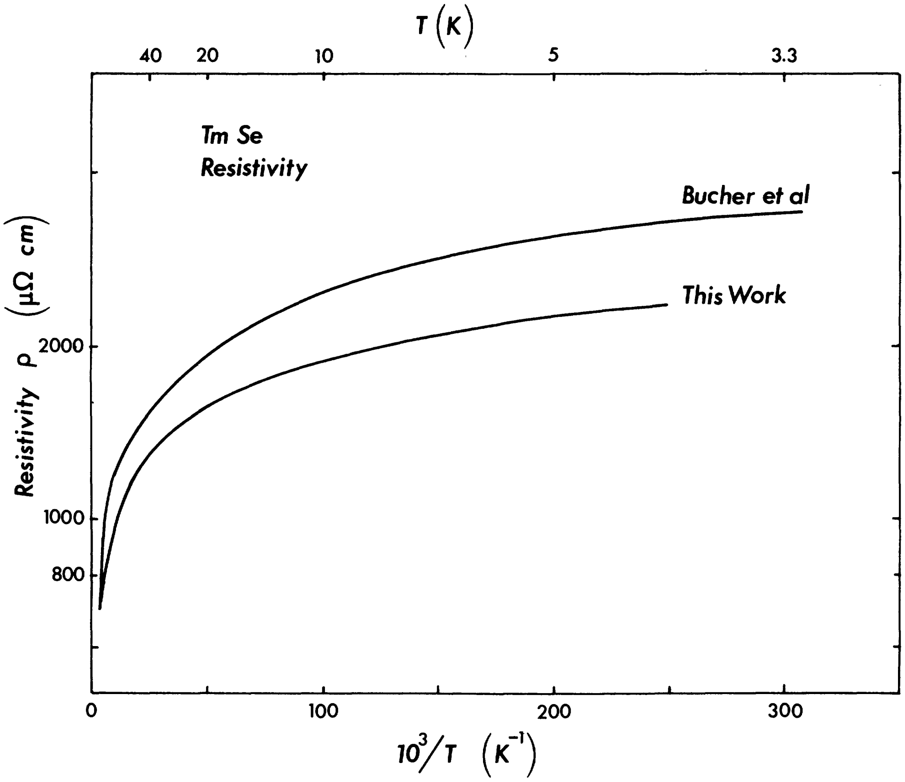

FIG. 3. dc resistivity of TmSe as a function of T^{-1}.

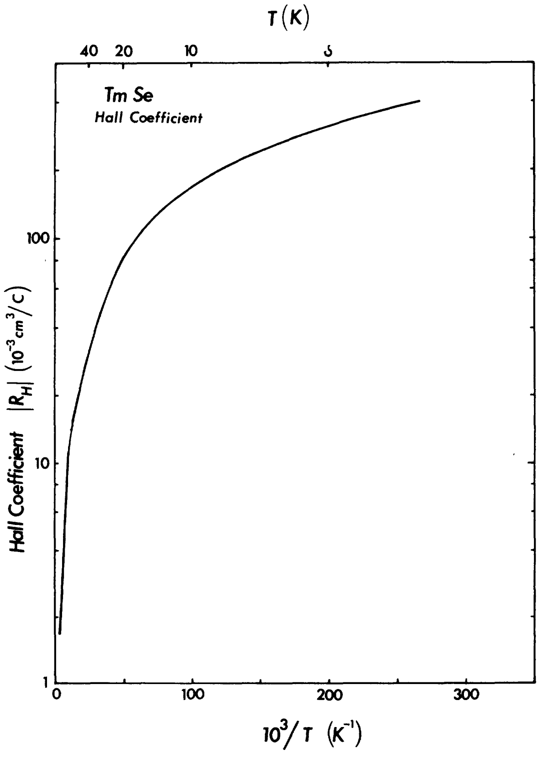

FIG. 4. Hall coefficient of TmSe as a function of T^{-1}.

portional to T^{-1}. The Hall coefficient R_H as a function as sample temperature is presented in Fig. 4; at all temperatures $R_H < 0$.

c. TmS. The polycrystalline samples of TmS had a lattice constant of 5.45 ± 0.02 Å and were golden in color. The room-temperature resistivity was 100 μΩ cm; the full temperature dependence is shown in Fig. 5.

IV. REFLECTIVITY

The analysis of the reflectivity was complicated by the cavity geometry used to accentuate the magnitude of the observed effects. An approach suggested by Allen[11] was used to determine R, the sample reflectivity, from the measured intensity ratio, P_s/P_r, arriving at the detector from the sample and reference cavities, respectively. For highly reflecting samples covering area A_1 in a cavity with small input and output holes each of area a,

$$P_s/P_r = 2a/[(1-R)A_1 + 2a]\,. \quad (1)$$

This expression was used to determine the sample reflectivity from the measured data for TmSe and TmS, since both are highly reflecting (>80%).

a. TmTe. TmTe was found to have very low reflectivity over most of the spectral range. As

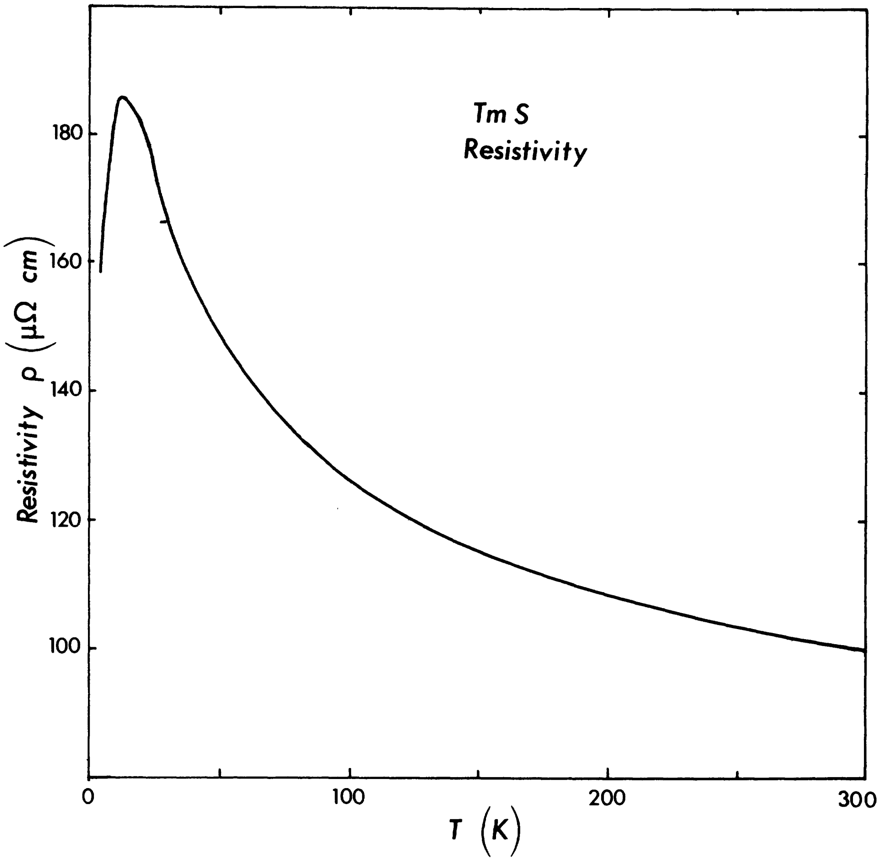

FIG. 5. dc resistivity of TmS as a function of T.

the data presented in Fig. 6 show, there is a strong reststrahlen peak in the neighborhood of 120 cm^{-1}. The exact frequency dependence of the reflectivity cannot be determined from our data because Eq. (1) is not applicable to materials of low reflectivity. Single reflection measurements had insufficient signal-to-noise ratio to obtain accurate spectra. The only strongly temperature-dependent aspect of

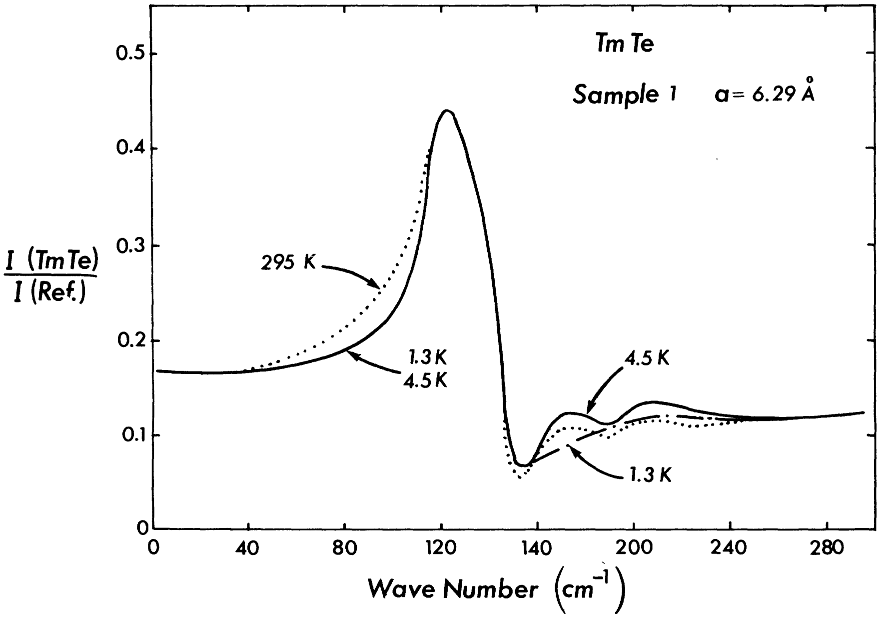

FIG. 6. Far-infrared reflection spectra of TmTe Sample 1 at three temperatures. The ratio $I(\text{TmTe})/I(\text{Ref})$ is the ratio of the intensity leaving the sample cavity to that leaving the reference cavity; it is the same ratio as given by P_s/P_r in Eq. (1).

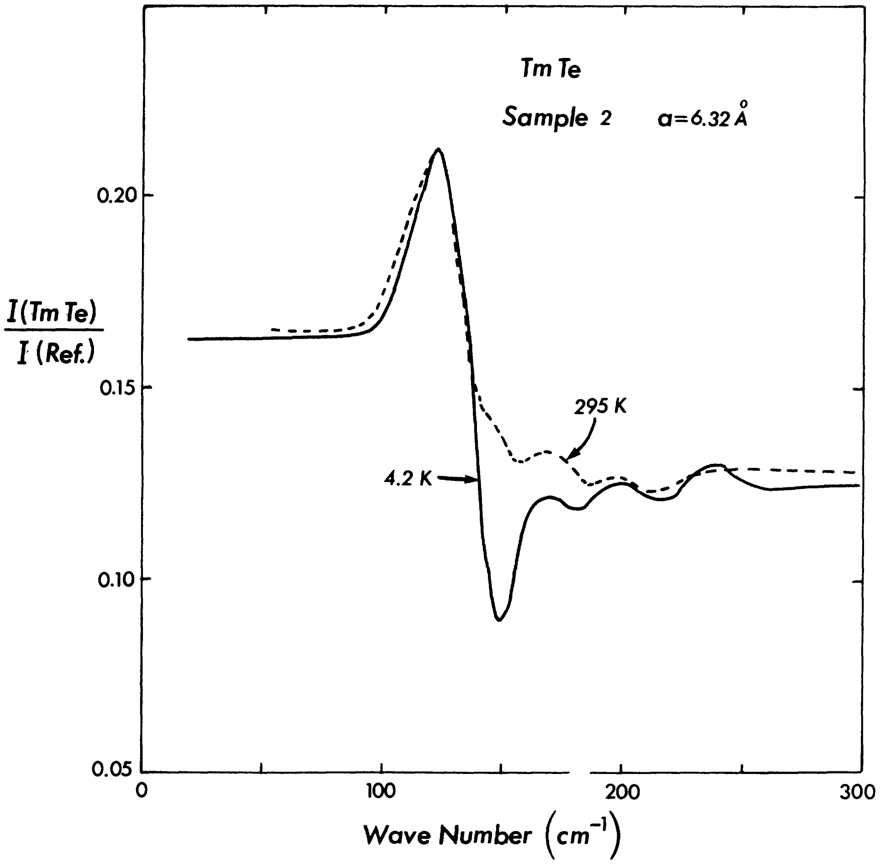

FIG. 7. Far-infrared reflection spectra of TmTe Sample 2 at two temperatures. The ratio I(TmTe)I (Ref) has the same meaning as in Fig. 6.

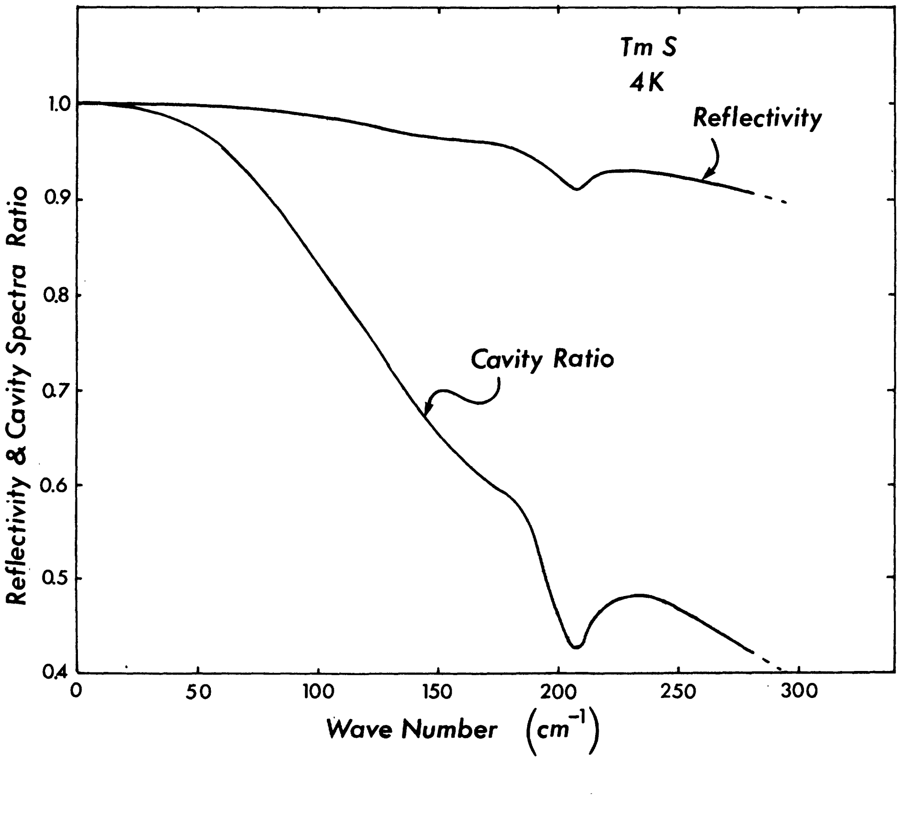

FIG. 8. Far-infrared reflectivity of TmS at 4 K and the ratio of cavity spectra from which it was derived.

the reflectivity spectrum is the appearance of two new features (at ~173 and ~209 cm^{-1}) as the sample temperature is increased from 1.3 to 2.5 K. These features persist up to room temperature, while the reststrahlen peak broadens slightly.

A second sample of TmTe produced the spectrum shown in Fig. 7. The 4.2-K spectrum is qualitatively similar to that of the other sample, with the exception of an additional peak at 238 cm^{-1}. However, the temperature dependence is quite different: (i) the structure between 160 and 260 cm^{-1} does not change as the sample is cooled to 1.3 K; (ii) this structure does change significantly as the sample is heated to room temperature. In addition, although the reflectivities above and below the reststrahlen peaks are approximately the same, the strength of the peak in the second spectrum is much less than in the first. The sample surface area exposed to the cavity was approximately the same for both samples, so the difference in strength is not merely an experimental artifact.

b. TmSe. The reflectivity of TmSe is high and monotonically decreasing in the far-infrared. It is nearly 100% at ~100 cm^{-1}, decreasing monotonically to ~90% at 400 cm^{-1}. Cavity effects prevent precise determination of the frequency dependence. The values reported by us earlier, which showed a strong frequency dependence, were incorrect due to an erroneous interpretation of the effects of the cavity. The temperature dependence of the spectrum is slight.

c. TmS. In Fig. 8, we show the reflectivity spectrum of TmS at 4 K; also shown is the ratio of cavity outputs used in Eq. (1) to calculate the reflectivity. The reflectivity is high and decreases with increasing frequency. However, between 160 and 260 cm^{-1}, there is structure which interrupts the smooth downward trend. The overall shape of the spectrum and the structure upon it are independent of temperature up to 85 K; room-temperature data show a slight decrease in overall reflectivity, but no significant change in the structure.

V. DISCUSSION

a. TmTe. The high dc resistivity and low infrared reflectivity of our samples are consistent with divalent Tm. However, the resistivities of our samples and especially their temperature dependences differ markedly from what is expected for a simple semiconductor. In addition, the infrared reflectivity spectra and their temperature dependences differ from that expected from a semiconductor. We shall examine our data in an attempt to find a consistent explanation of their properties.

The two samples studied in this laboratory show resistivities which differ significantly from each other and from that reported by Bucher *et al.*[1] The three samples also differ in lattice constant. There is no systematic variation of ρ(300 K) with lattice constant. Differing low concentrations of ionized impurities may contribute to the conductivity. However, it is clear from the data in Fig. 1 that, as the lattice constant decreases, the large rise in resistivity occurs at lower temperatures. This is consistent with the presence of increasing amounts of Tm^{3+} (resulting from interconfiguration fluctuations) as "defects," persisting to contribute to the conductivity until "frozen out" at low temperature where the divalent state is favored. It is not possible to fit the extremely rapid low-temperature rise in resistivity in Sample 1 to a thermal activation model. From lattice-constant considerations, we can estimate that, if the sample studied by Bucher *et al.*[1] has Tm with valence 2.00, Sample 1 has a valence ~2.12 and Sample 2 has a valence ~2.05 at room temperature. No lattice-constant measurements have been performed at low temperatures, but such measurements could provide important information about the existence of a preferred divalent state at low temperatures.

All three samples show linear dependence of ln ρ upon T^{-1} near room temperature. However, the activation energies implied by the slopes of the plots between 300 and 200 K, based on a simple thermal activation model, differ by up to a factor of 10! We conclude that the intrinsic conductivity in this range is probably thermally activated but that the energy gap is very sensitive to slight changes in lattice constant and/or stoichiometry.

The low-temperature reflectivity data are also consistent with predominantly divalent Tm. The reststrahlen bands which dominate the spectrum of both samples occur at the frequency expected from comparison with the divalent Eu chalcogenides[12,13] for a divalent lattice.

Both of our samples show additional structure on the high-frequency side of the reststrahlen band. In our $a = 6.29$ Å sample, this structure vanishes when the sample is cooled below 2.5 K; this is the temperature at which the rapid 10^3-fold rise in resistivity occurs. The extra structure is probably due to resonances in the vibrational motion of the Tm^{3+} "defects" which should be bound more strongly to the lattice than Tm^{2+} and hence have higher vibration frequencies. The large width of these resonances may be due to strong coupling between the vibrational motion and the temporal fluctuations in valence. The characteristic linewidth of the resonances implies a time scale ~10^{13} sec.

Similar resonances are present in the spectra of our $a = 6.32$ Å at 4 K. These persist to the lowest temperatures reached (1.3 K); most of the structure also persists to room temperature. In addition, there is increased reflectivity around 150 cm^{-1} at room temperature. We suggest that this behavior is due to crystal imperfections such as internal strain and impurities. This is supported by our observations that cleaving this crystal was more difficult than cleaving the first sample and that the cleaved faces were not smoothly planar, but showed some distortion. The presence of strains would account for the broadened reststrahlen peak and defects could cause the additional high-frequency structure. Strains could also prevent the "freezing out" at low temperatures of the Tm^{3+} "defect ions" responsible for the reduced resistivity and for some of the optical structure.

We conclude that Tm in TmTe is predominantly divalent, but that the transport and optical properties are very sensitive to the degree of crystal perfection and to the presence of factors affecting lattice constant. In this case a likely factor is the presence of Tm^{3+} ions, resulting from interconfiguration fluctuations, acting as defects. We should emphasize that the absence of effects[6] attributable to interconfiguration fluctuations in crystals of good stoichiometry (±0.5%), whose lattice constant is 6.353 Å, suggests that the effects we have observed result from deviations from perfect stoichiometry.

b. TmSe. Our sample of TmSe exhibits a temperature-dependent resistivity similar to that observed by Bucher *et al.*[1] as seen in Fig. 3. The lattice constants of the samples measured at Bell Labs were 5.64–5.71 Å. The increase in resistivity with decreasing temperature cannot be fit by a thermal activation model. However, it does suggest reduction in the number of carriers present, which Bucher *et al.*[1] suggest may accompany an increasing favored divalent state at low temperatures. On the other hand, it is also consistent with the data presented by Berger *et al.*[7] and with the model which they propose. They attribute the increase in resistivity with decreasing temperature to Kondo[14] resistivity of Tm^{3+} ions. The spin-disorder coupling constant in Kondo's theory is strongly enhanced if the f-electron level is close to the Fermi level, as is believed to be the case in TmSe. This magnetic scattering is likely the dominant contribution to the low-temperature resistivity.

The Hall coefficient at 295 K is $(2.3 \pm 0.2)\times 10^{-3}$ cm^3/C. This implies an electron density (based on free-electron theory) of $n_H = (R_H e)^{-1} = (2.7 \pm 0.3) \times 10^{21}\ \mathrm{cm}^{-3}$. The density of Tm ions is $4[(5.64 \pm 0.02)\times 10^{-8}\ \mathrm{cm}]^{-3} = (2.22 \pm 0.03)\times 10^{22}\ \mathrm{cm}^{-3}$, implying that there are about 0.12 conduction electrons per Tm ion. This is consistent with the results of Berger *et al.*[7] However, free-electron theory is not appropriate to a system where strong magnetic scattering is present. Many years ago Kondo[14] pointed out that in rare-earth materials there can be skew scattering which will give rise to an extraordinary contribution to the Hall effect, especially when the f-electron level is close to E_F. This seems to be the most plausible explanation of the strong temperature dependence of the Hall coefficient.

It is interesting to note that for high magnetic fields at low temperatures Haen *et al.*[8] report that the Hall coefficient of TmSe is reduced markedly and saturates at a value that corresponds to approximately one conduction electron per Tm ion. Thus it appears that the anomalous contribution to R_H is suppressed by the high magnetic field. One conduction electron per Tm ion was also found by Batlogg *et al.*[6] by fitting the optical reflectivity. We conclude that there is most likely one conduction electron per Tm ion and that the resistivity and Hall coefficient are both strongly affected by magnetic scattering.

The reflectivity of TmSe is typical of that of a metal. No structure is observed in the frequency range studied and the data reduction process necessary to yield reflectivity values introduces sufficient uncertainty to prevent meaningful attempts at curve fitting to obtain optical constants. However, the level (~90%) at our highest frequencies is fully consistent with the measurements of Batlogg *et al.*[6] in their lowest-frequency region.

c. TmS. The room-temperature low resistivity and high reflectivity are typical of a metal. The temperature dependence of the resistivity is unusual, with a peak at 14 K. These results are almost identical to those obtained at Bell Labs on a sample with lattice constant 5.42 Å, and are similar to the results of Berger *et al.*[7] They observed a peak in ρ at ~10 K with a sample whose lattice constant is also 5.42 Å. The peak in the resistivity is quite different from that which occurs in EuS.[11] In that compound, the resistivity peak value is $\sim 4000\rho(300)$ and occurs close to the Curie temperature $T_C = 16.3$ K. In TmS, the magnetic phase transition[1] is $T_N = 5.2$ K, far from the peak in resistivity at 14 K. No large anomaly is present at the ordering temperature. The origin of the peak most likely lies in the same magnetic scattering of conduction electrons as discussed above for TmSe. Berger *et al.*[7] attribute the peak to thermal depopulation of the excited levels as the temperature is decreased.

The reflectivity spectrum has a high overall level typical of a metal. Our data agree with those of Batlogg *et al.*[6] in the region of overlap. The weak additional structure at 190 cm^{-1} bears close examination. It is suggestive of a reststrahlen band with frequency $\omega_{TO} = 180 \pm 5\ \mathrm{cm}^{-1}$. A plot of the lattice-constant dependence of the known phonon frequencies of the europium chalcogenides and EuO indicates that if TmS were divalent, we should expect the transverse optical phonon frequency in the neighborhood of 280 cm^{-1}. The phonon frequencies in the trivalent compound should be significantly lower due to the "softening" effects resulting from screening by the conduction electrons. Hence the peak observed in TmS can serve as further confirmation of the trivalent nature of the compound. The observation of structure in TmS and not in TmSe is surprising in view of TmSe's lower dc conductivity and lower reflectivity.

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