FREQUENCY DEPENDENT CONDUCTIVITY IN HfTe$_5$ AND ZrTe$_5$

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We report the observation of strongly frequency (ω) dependent
conductivity $\sigma(\omega)$ associated with the resistivity anomalies in HfTe$_5$ and
ZrTe$_5$. Much weaker ω dependence was found in the alloy Hf$_{0.5}$Zr$_{0.5}$Te$_5$.
We suggest that the ω dependent conductivity is due to the dynamical
response of a collective mode.

The linear chain compounds HfTe$_5$ and ZrTe$_5$ show large resistivity peaks at temperatures below room temperature.[1,2] The resistivity peaks and anomalies of the thermoelectyric power and Hall coefficient[3] are reminiscent of observations in linear chain[4-6] or layer compounds,[7,8] where second order structural phase transitions occur. The source of such phase transitions in most of these cases has been established as a charge density wave (CDW). However, detailed transport and magnetic measurements in the pentatellurides failed to show a sharp phase transition, and efforts to observe the appearance of superlattice reflections due to the periodic lattice distortion near to the temperature where the anomalies are observed were unsuccessful.[9] A supperlattice was found at room temperature, where the resistivity shows metallic behavior,[9] and the intensity of the X-ray peaks associated with this distortion shows a weak increase at low temperatures.[10]

In this communication we report the observation of strongly frequency (ω) dependent conductivity $\sigma(\omega)$ in the temperature region where the anomalies are observed. The resistivity anomaly is nearly completely wiped out both in HfTe$_5$ and in ZrTe$_5$ at microwave (9.1 GHz) frequencies. A smaller effect is observed in a Hf$_{0.5}$Zr$_{0.5}$Te$_5$ alloy, showing that disorder leads to the suppression of the strong frequency dependence. These observations are similar to those obtained on the layer compound TiSe$_2$,[11] where the appearance of a commensurate superlattice at a second order phase transition is responsible for the resistivity anomaly. We suggest that $\sigma(\omega)$ reflects the response of a pinned collective mode, and compare our findings with those made on the linear chain compounds NbSe$_3$ and TaS$_3$.

The conductivity at 9.1 GHz was measured by a cavity perturbation technique.[12] In this method the conductivity and dielectric constant are obtained from the observed frequency shift and change of absorption of the microwave cavity. When the conductivity is large (the so-called metallic limit) the shift is determined only by the sample dimensions, and the conductivity can be determined from the absorption. For the HfTe$_5$, ZrTe$_5$, and alloy samples, the shift corresponds to that evaluated from the measured sample dimensions, and we conclude that the metallic limit is appropriate in our experiments. The 2.4 GHz conductivity was measured with an HP network analyzer, and special care was taken to avoid spurious effects associated with improper matching conditions. A two probe configuration with indium solder contacts was used. While this configuration leads to noticeable dc contact resistances at low temperatures, at high frequencies we have found that contact problems are negligible, most probably due to the capacitive coupling associated with the contacts. The samples used in this work were from the same batches as those on which resistivity and susceptibility measurements were reported earlier.[9]

Figure 1 shows the resistivity, normalized to the room temperature value, at dc and high frequencies. The dc resistivity was taken from earlier measurements on samples taken from the same preparation batch, and the dc error bars represent the variation of the dc resistivity data from sample to sample.[9] The full and open circles represent the result of microwave experiments on two samples with different sample dimensions, and demonstrate the validity of the evaluation of the conductivity from the measured absorption. It is evident from Fig. 1 that while there is no observable frequency dependence at high temperatures where the resistivity shows a metallic behavior, the resistivity anomaly is nearly completely removed at microwave frequencies. At low temperatures the resistivity again appears to be independent of the frequency. The data taken at 2.4 GHz are between the dc and 9.1 GHz resistivities in ZrTe$_5$ and in the alloy Hf$_{0.5}$Zr$_{0.5}$Te$_5$. While the resistivity anomaly is clearly suppressed in ZrTe$_5$ (the effect is nearly as strong as in HfTe$_5$) only a weak suppression is observed in the alloy. In fact, for this latter case, the difference between the dc and 9.1 GHz data is within the experimental error.

We first note that our observations are closely similar to those found in the layer compound TeSi$_2$.[11] In this compound, the hexagonal a and c axis parameters double to
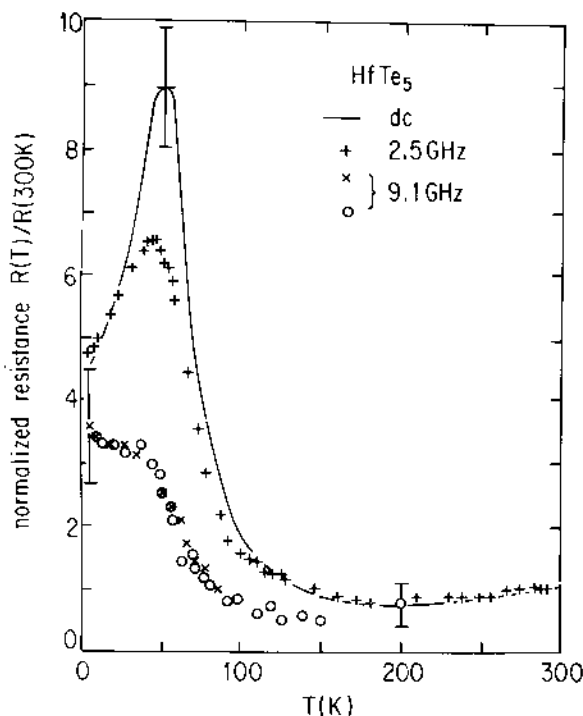
Fig. 1. Temperature dependence of the resistivity of $HfTe_3$ at various frequencies. The dc error bar represents the variation of the dc resistivity maximum from sample to sample.

form a simple superlattice below a second order phase transition at 202 K. The pentatellurides have a structure consisting of chains of MTe_3 joined by Te chains along one direction.[13] The conductivity is approximately the same parallel and (along the direction joined by the Te atoms) perpendicular to the chains.[14] These observations, together with band structure calculations,[15] strongly suggest that $HfTe_5$ and $ZrTe_5$ are more properly viewed as 2D materials. Moreover, such calculations show that the material is semi-metallic, with the holes and electrons having primarily Te character. Similar resistivity anomalies are associated with the frequency dependent transport in $TiSe_2$ and, moreover, the observed frequency dependence is also strongly reduced by disorder effects. We believe, therefore, that a proper account for the experimental observations should include the 2D character of these compounds. The other comment we make is that the energy $\hbar\omega$ associated with the measuring frequency is orders of magnitude smaller than the thermal energy kT. The temperature T = $\hbar\omega/k$ corresponding to 9.1 GHz is 0.3 K while the resistivity anomalies occur at much higher temperatures. If the frequency dependent transport we observe would reflect single particle transport, then the removal of the resistivity anomaly would require a strongly energy-dependent density of states, or scattering processes. These, however, would also be wiped out by thermal broadening. We conclude, therefore, that the strong frequency dependence observed at high temperatures is not compatible with a single particle transport phenomenon.

The most likely explanation of our experimental findings is that the resistivity anomalies are associated with the development of a collective mode, and the frequency dependent conductivity is due to the response of the collective mode to external ac driving fields. The strong increase of the dc resistivity is then due to the freezing out of the normal electrons, which are condensed in the collective mode. Due to the 2D character, only part of the Fermi surface is removed, leading to a finite resistivity, as in other layer compounds and in the linear chain compound $NbSe_3$.[4] The collective mode is pinned by impurities or by the underlying lattice and thus does not contribute to the dc conductivity. Because of the large number of electrons condensed into a collective mode, the condensate is stable at high temperatures, but a small restoring force (on a one-electron basis) may lead to a strongly frequency dependent response. While the existence of this collective mode implies a phase transition, no solid evidence for the nature of this phase transition is presently available. At present lack of diffraction evidence for a CDW[9] or NMR evidence for a Spin Density Wave[16] makes this an interesting puzzle indeed.

In the linear chain compounds $NbSe_3$ and TaS_3, this frequency dependent response is described phenomenologically by a harmonic oscillation with an inertia and with a restoring force ω_0^2. σ increases from dc to microwave frequencies, suggesting a strongly overdamped response. The crossover frequency $\omega_{c.o.} = \omega_0^2\tau$ is approximately 3×10^8 sec^{-1} for $NbSe_3$ below the second CDW transition and 10^9 sec^{-1} for TaS_3 in the CDW state.[17] This approach may be appropriate for $HfTe_5$ and $ZrTe_5$ and the smooth increase of σ with increasing frequency then again suggests an overdamped response. A weak restoring force also suggests that the collective mode can be depinned by moderate dc electric fields. Indeed, strongly nonlinear conduction was found in $NbSe_3$ above 10 mV/cm[18] and above 1 V/cm in TaS_3.[19] No nonlinear conductivity was found in the pentatellurides up to 1.5 V/cm.[9] This suggests that, if the same model is applied for the tri- and pentachalcogenides, the strong frequency dependence of the latter compounds is due to the strong damping or large damping time τ.

In conclusion, we have observed strongly frequency dependent conductivity associated with the resistivity anomalies of $HfTe_5$ and $ZrTe_5$. This and the strong suppression of the frequency dependence by disorder strongly suggest that $\sigma(\omega)$ reflects the dynamical response of a collective mode. We also note the strong similarity of $\sigma(T)$ and $\sigma(\omega)$ between $TiSe_2$ and the pentatellurides. While a commensurate phase is clearly associated with these observations in $TiSe_2$, further studies are required in $HfTe_5$ and $ZrTe_5$ to establish the nature of the probable phase transitions at low temperatures.

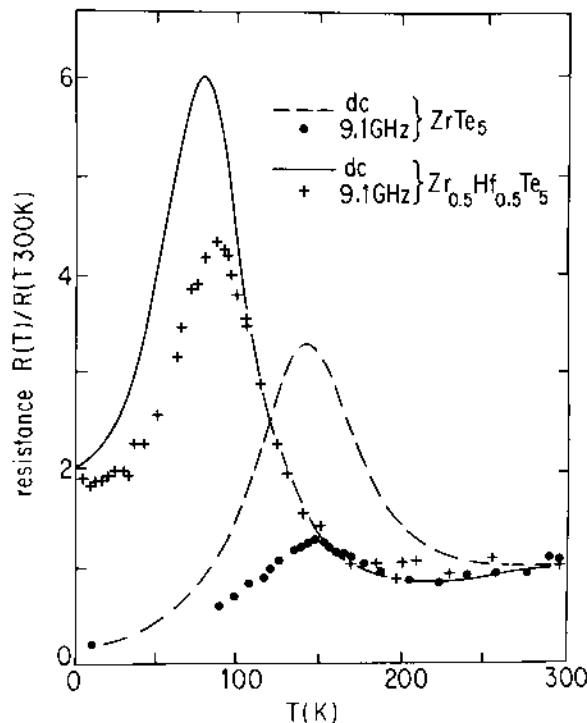Fig. 2. Temperature dependence of the
resistivity of ZrTe$_5$ and Zr$_{0.5}$Hf$_{0.5}$Te$_5$
at dc and at microwave frequencies.

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