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H. Mutka [a] & A. Meerschaut [b a]

[a] Section d'Etude des Solides Irradiés Centre d'Etudes Nucléaires, B.P. N°6 - F-92260 Fontenay-aux-Roses, France

[b] Laboratoire de Chimie des Solides, Université de Nantes 2, Rue de la Houssinière - 44702, Nantes, Cedex, France

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THERMOPOWER AND IRRADIATION INDUCED DISORDER IN MONOCLINIC TaS_3

H. MUTKA
Section d'Etude des Solides Irradiés
Centre d'Etudes Nucléaires
B.P. N°6 - F-92260 Fontenay-aux-Roses (France)

A. MEERSCHAUT
Laboratoire de Chimie des Solides
Université de Nantes
2, Rue de la Houssinière - 44702 Nantes Cedex(France)

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The thermopower of monoclinic TaS_3 shows that the charge-density-wave driven metal-insulator transition at 160 K is comparable to the Peierls transitions in organic conductors. However, the insulating low temperature state with thermally activated conductivity is quite unsensitive to irradiation induced disorder. Instead the disorder pushes the insulating properties up to higher temperatures, in samples with about 10^{-2} at.fraction of defects the conductivity is activated and the thermopower has a 1/T dependence in all the measured range from ~ 60 to 300 K.

Monoclinic TaS_3 is the structural analogue of the well-known Charge-Density Wave compound $NbSe_3$: they have both a chain-like structure of metal atoms in chalcogen prisms[1]. Consequently they are anisotropic metals, a feature essential for the forming of Charge Density Wave (CDW) distortions[2].

Of these two the TaS_3 has far more anisotropic electronic properties, the conductivity anisotropy is of the order of 10^2 (σ along the chains/ σ transverse)[3] instead of ~ 10 in $NbSe_3$[4]. This anisotropy is also reflected in

the CDW instability : in TaS_3 structural precursor effects are visible above the phase transitions[1] as it is typical of quasi-one-dimensional systems like the organic metals with CDW (Peierls) distortions[5]. In fact, like the organic conductors the monoclinic TaS_3 is driven by the CDW to an insulating state at low temperatures. This metal-insulator transition happens at 160 K and it is well visible in the resistance curve 1 of Fig. 1. Already at 240 K another

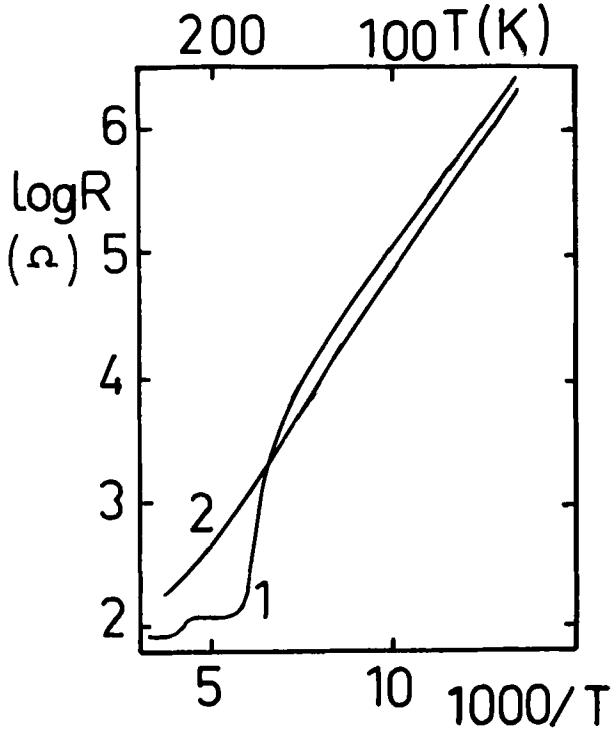

FIGURE 1. The resistance of pure monoclinic TaS_3 (curve 1) shows the metal-insulator transition at 160 K. Another anomaly is seen at 240 K. The same sample, now containing 10^{-2} at fraction of displaced Ta has no more transitions but the activated low temperature behaviour remains unchanged (curve 2).

phase transition is observed with a less important anomaly. In the monoclinic TaS_3 as well as in $NbSe_3$ the lattice distortions are incommensurate, deviating slightly from a

commensurability of order four. All structural evidence on the phase transitions in TaS_3 and $NbSe_2$ is presented in ref. 1 and compared to those observed in the orthorhombic variety of TaS_3.

The quasi-one-dimensional conductors are usually very sensitive to disorder. The Peierls-transition can be suppressed by a concentration of a few 10^{-3} of for example irradiation induced defects[6]. At such levels of disorder one can also observe the suppression of the collective paraconductivity due to the sliding CDW[7]. The remarkable non-linear properties of $NbSe_3$ can also be affected by irradiation induced disorder[8]. All these effects are due to the pinning of the CDW distortion on the defects[6].

As to the sensitivity to the perturbation due to defects the monoclinic TaS_3 makes no exception. In the first irradiation study[3] the following observations were made :

i/ the most effective defects are created by displacing Ta atoms. The fraction of Ta displaced under irradiation can be well estimated.

ii/ at defect concentrations exceeding a few 18^{-3} displaced Ta the CDW is completely pinned to defects. Even at the lowest temperatures no long-range ordered state is obtained. Instead electron diffraction shows that the distortion is present without transverse coherence, like in the pure material above the ordering transitions. This structural evidence of the pinning is discussed in ref. 9.

iii/ even though the insulating low temperature properties seem to be associated with the ordering of the CDW they are not destroyed by the pinning. This is shown by the resistance curve 2 in Fig. 1 that was measured for a sample containing 10^{-2} at. fraction of displaced Ta. The absolute value as well as the activation energy of the conductivity are little or not at all affected at temperatures below the metal insulator transition.

This puzzling conductivity behaviour of irradiated TaS_3 is strongly in contrast with all the organic Peierls systems studied up to now[10] as well as any classical semiconductor[11]. It was even questioned if it is a consequence of an inhomogeneous but anyhow microscopically metallic character of the samples[3].

The answer is given in the present study of thermopower. This transport property shows clearly that the metal-insulator transition is a microscopic property of

TaS_3 and that the semiconductor-like transport is stabilized by irradiation induced disorder.

The crystals of TaS_3 were grown by the iodine transport method and checked with X-rays for the monoclinic structure. Being small in cross-section (a few tens of μm^2) and relatively long (~ 1 mm in the direction of the conducting chains) the crystals are quite suitable for thermopower measurements. The thermopower was measured in an apparatus equivalent to that described by CHAIKIN and KWAK[12]. The apparatus has been checked on organic quasi-1-D conductors that gave results consistent with literature data[13].

The absolute thermopower of TaS_3 (the measured thermopower minus the absolute thermopower of gold[14]) is presented by curve 1 in Fig. 2. For the pristine sample the value at high temperature is very small, of the order of 1 $\mu V/K$. The thermopower is negative around room temperature, at the phase transition at 240 K we observe a change of sign. Down to 160 the thermopower is small and has little temperature dependence. These facts are consistent with the metallic behaviour of the resistivity.

Another change of sign with a spectacular increase of the absolute value of thermopower is observed at 160 K. This sudden increase is quite analogous with the behaviour of the organic conductors at the Peierls transition[15]. A value of nearly - 100 $\mu V/K$ is reached below 100 K before the measurement becomes impossible due to the high impedande of the sample.

Such an increase of the absolute value of the thermopower confirms the microscopic character of the low temperature insulating phase. A thermally activated behaviour of resistivity can be observed in an inhomogeneous (granular) metal, especially in quasi 1-D systems, but the thermopower is less sensitive to inhomogeneities because no current flow is needed[16].

This is clearly demonstrated by FORRO[17] who has measured the thermopower of irradiated organic conductors. These are systems of metal segments and have a thermally activated conductivity but the thermopower is typically metallic, it is small and extrapolates to zero at decreasing temperature. Similar observations of a small thermopower on a sample whose resistivity has a tendency to increase with decreasing temperature have been reported irradiated $NbSe_3$[18,19].

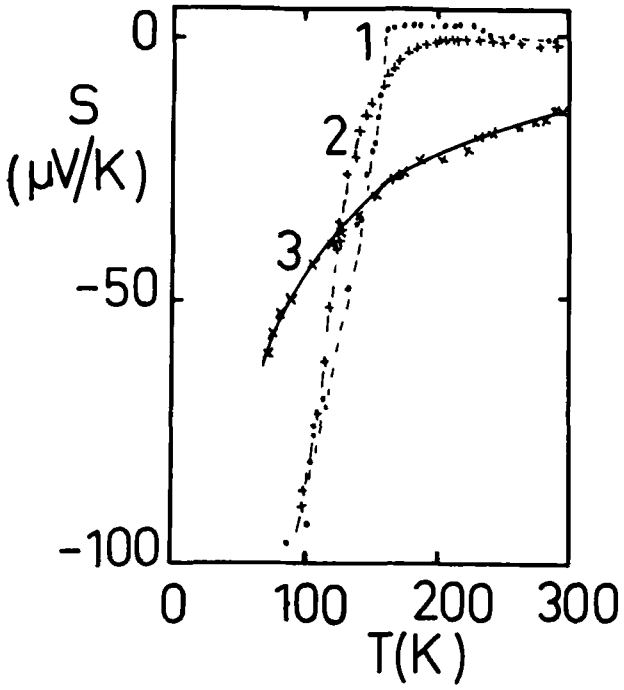

FIGURE 2. The thermoelectric power of pure monoclinic TaS_3 shows a sudden drop at the metal-insulator transition (curve 1). After irradiation the sample to a dose corresponding to $5x10^{-3}$ displacement Ta the sharp transitions are lost (curve 2). Another, more irradiated sample (2.10^{-2} disp. Ta) shows a 1/T temperature dependence (curve 3, full line).

After irradiation to a dose corresponding $5x10^{-3}$ displaced Ta a suppression of the sharp phase transitions is manifest, see curve 2 in Fig. 2. The thermopower has a value of ~ - 3 μV/K at room temperature. Passing close to zero it turns down to reach once again a value of - 100 μV around 100 K.

The most irradiated sample containing $2x10^{-2}$ of displaced Ta has no more transitory behaviour. The thermopower is relatively large already at room temperature (- 14 μV/K) and it decreases following a 1/T dependence consistent with semiconducting transport mechanism by activation across a band gap[20] or to a mobility edge[21].

The results presented above show clearly that in monoclinic TaS_3 there exists a semiconducting like low tem-

perature phase and that it is stabilized by disorder up to room temperature. This stabilization of the insulating properties is strongly in contrast with the behaviour of the organic Peierls-system where the metallic properties are stabilized by disorder. The apparent insensitivity of both the activation energy and the absolute value of the conductivity does not fit in a classical semiconductor scheme either. Even ignoring the microscopic properties of the irradiation induced defects it is difficult to imagine a situation with perfect compensation and no change in activation energy.

A more exotic possibility, consistent with the diffraction study[9], would be the creation of localized phase defects of the lattice distortion that are bound to atoms displaced by irradiation or to vacant lattice sites. The electronic properties of such soliton defects have been studied in model systems[22,23] and applied to doping of polyacetylene[22]. No theory applicable to TaS_3 has been made yet. WILSON[24] has proposed that such defects could explain the apparent non-commensurability of the lattice distortion in $NbSe_3$, consequently as well in TaS_3. Such inherent defects might explain the insensitivity of the low temperature phase of TaS_3 to disorder.

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