PROPERTIES OF THE STRUCTURAL PHASE TRANSITION IN THE CHAIN SEMICONDUCTOR $(NbSe_4)_3$ I

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Abstract

Results of thermal conductivity, thermopower, dc electrical resistivity and thermal capacity measurements on the linear chain semiconductor $(NbSe_4)_3I$ *around the structural phase transition at* $T_p = 274$ *K are presented. Apart from the cleary visible consequences of the phase transition in all properties we also report on the anomalous behaviour of thermal conductivity as well as some hysteretic behaviours below* T_p.

The new class of halogenated transition-meta tetrachalcogenides with the general formula $(MX_4)_nY$ (M = Nb, Ta; X = S, Se; Y = halogen n = 2, 3, 10/3,4) provide good examples of systems with restricted dimensionality exhibiting interesting phase transitions. This has been extensively investigated in the last few years because some of those systems show charge density wave (CDW) formation and nonlinear transport properties ascribed to Fröhlich-type conduction when the CDW becomes unpinned and moves through the crystal.

The pseudo-one-dimensional character is due to a peculiar structure of these compounds. The crystal consists of parallel MSe_4 chains which are well separated from one another by halogen atoms. Along each MSe_4 chain the metal atoms are located at the centers of rectangular antiprisms of eight Se atoms. The d_z2 band filling of metal atoms changes with composition (n) leading to different structural and electrical properties: $(TaSe_4)_2I$ and $(NbSe_4)_{10/3}I$ undergo a Peierls transition, while $(NbSe_4)_3I$ exhibits different structural phase transitions(1).

The aim of our work was to measure thermal conductivity, thermal capacity, thermopower and dc resistivity of $(NbSe_4)_3I$ to see how the structural phase transition at $T_c = 274$ K influences these properties. Recent results of electron diffraction(2), X-ray(3) and Paman(4) scattering experiments show that this transition is a second-order displacive one. Below T_c two neighboring chains are shifted with respect to each other changing the metalic seguences on them.

The results of our dc conductivity measurements (Fig. 1.) show that the behaviour of our samples places them betwen type I and type II. There is a gap of 4000 K around room temperature which sharply decreases at the phase transition temperature because of a greater delocalization of electrons along the chain. The change of the slope below 200 K indicates the existence of a third type of behaviour which could be described as a mixture of type I and type II.

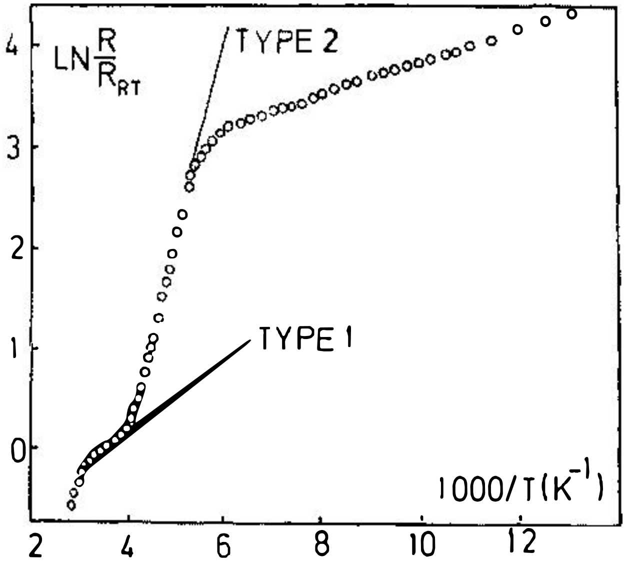

Fig. 1. DC electrical resistivity versus 1000/T has at lower temperatures behaviour between type I and type II.

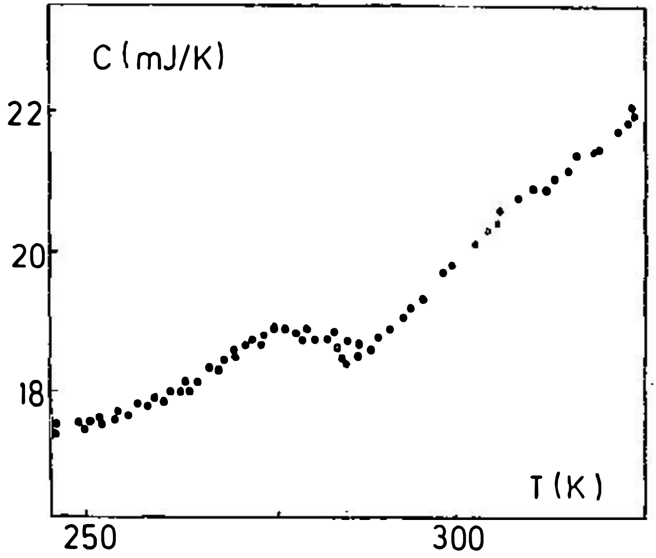

Fig. 2. Thermal capacity of the $(NbSe_4)_3I$ sample. The contribution of the sample holder has not been substracted.

The existance of the phase transition is clearly visible in the thermal capacity Fig. 2. We observed no latent heat associated with the phase transition.

Figure 3. shows the temperature behaviour of the anisotropy in dc resistivity with an abrupt change around 200 K and a significant thermal hysteresis from room temperature to 200 K.

The results of high resolution thermal conductivity measurements are show in Fig. 3. The thermal conductivity of the lattice is much higher than the one due to electrons, so we can conclude that the change in slope at 275 K is a consequence of a structural phase transition. The hysteresis we observed on heating is depends sensitively on the thermal treatment of the sample.

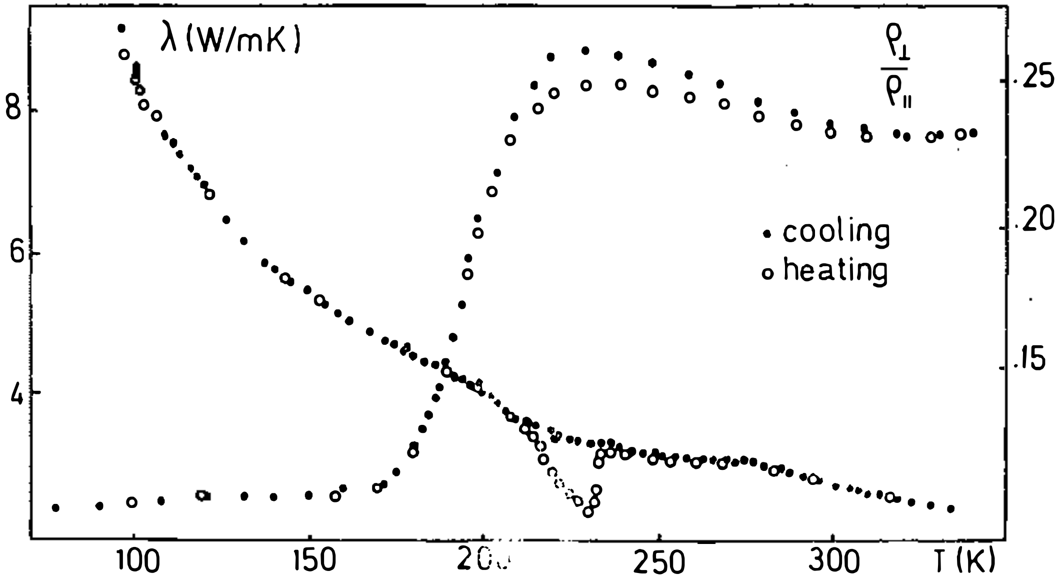

Fig. 3. Thermal conductivity of $(NbSe_4)_3I$ sample as well as conductivity anisotropy in the same temperature region show hysteretic behaviour below the phase transition.

The thermopower in the chain direction has a temperature dependence similar to that of the resistivity (Fig. 4.). Above the phase transition it has an activated form. Below T_p it is constant and below 120 K it becomes again weakly activated. It the transverse direction it is 50% smaller and below T_p it decreases slightly on farther cooling. The negative sign shows that the charge carriers are predominantly electrons.

Cur results confirm the existence of the structural phase transition at 274 K. Moreover, some hysteretic behaviours has been observed. The posible explanation could be that there is a coupling of at least two phase orderings: the first one at 274 K connected with a rotation of the selenium rectangles and the second one with a change in Nb-Nb distances. The other explanation could be related to the metastable states associated with the interplay of crystal defects and the structural phase transition.

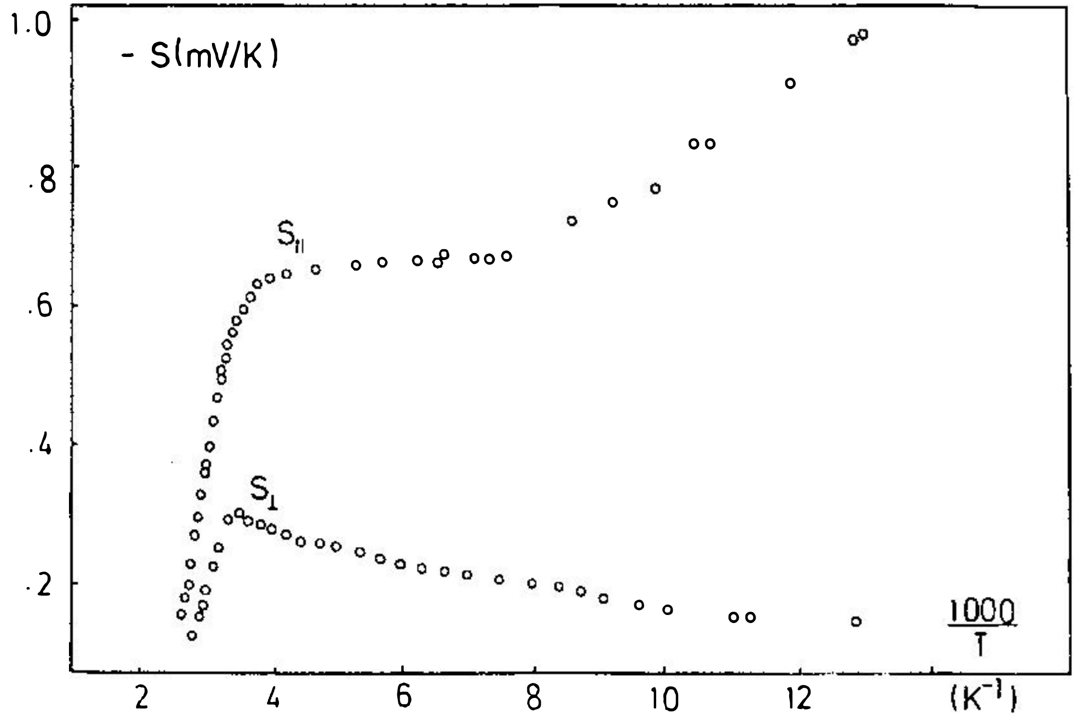

Fig. 4. Thermopower versus 1000/T measured in the chain direction and perpendicular to the chains shows different behaviour at lower temperatures.

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