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Thermopower and resistivity of $K_{0.3}MnO_3$ and $Rb_{0.3}MnO_3$

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We report on very precise measurement of thermopower and resistivity of K-and Rb- blue bronze, $K_{0.3}MnO_3$ and $Rb_{0.3}MnO_3$. We have found that, as in $K_{0.3}MnO_3$, there exists a deep low temperature minimum in the thermopower of $Rb_{0.3}MnO_3$. There are some indications that it is due to phonon drag. However, it is interesting that the low temperature behaviour of the thermopower can be correlated to the resistivity. This correlation can explain why the thermopower does not follow simple $1/T$ behaviour above the minimum. Owning to our precise measurements, we are able to determine the temperature of the phase transition, T_P, by the thermopower as well as by the resistivity data. The extracted values give that T_P is 177.5 K for $K_{0.3}MnO_3$ 177.8 K for $Rb_{0.3}MnO_3$, i.e. the same value within the errors of the measurements.

The molybdenum blue bronze compounds $A_{0.3}MoO_3$ (A= K, Rb, Tl), the quasi-one-dimensional (Q-1D) compounds which undergo the Peierls transition at about 180 K, have been investigated for a long time. However, a complete physical picture is not established yet and, moreover, there still left some not yet measured experimental facts. Here, we present, besides some others interesting points, the low temperature thermopower of $Rb_{0.3}MoO_3$. As well known, it is very difficult to get the precise data of the low temperature thermopower of the Q-1D compounds and, moreover, below certain temperature the thermopower cannot be measured at all, as already pointed but never discussed the reasons for that [1]. Recently, we succeeded to measure successfully the thermopower of TaS_3 below 50 K down to about 25 K [2] and, here, we present the thermopower of $Rb_{0.3}MoO_3$ measured down to 37 K. For comparison, it was measured by the same experimental apparatus and in the same manner the thermopower of $K_{0.3}MoO_3$ [3]. We revealed that, as in $K_{0.3}MoO_3$ and TaS_3, there exists a deep low temperature minimum in the thermopower of $Rb_{0.3}MoO_3$. This extreme in the thermopower, much larger than in metals could be, is one of the indications of semiconducting character of the low temperature phase and it is ascribed, usually, to the phonon drag effect [4]. However, some authors try to connect the extremes in the thermopower to the open gap on the Fermi surface introduced by charge density waves formed at the transition [5]. It is difficult to resolve these two effects because in both cases, according to theory, the thermopower should obey $1/T$ behaviour.

Fitting the data above the minimum but below transition temperature, T_P, to function:

$$A/T + BT \qquad (1)$$

one obtains: for $K_{0.3}MoO_3$: A = -23948 μV and B = +0.682 μV/K^2 in the temperature interval: 115 K < T < 159 K. This result is in agreement to the results found in literature concerning the order of magnitude [4]. For $Rb_{0.3}MoO_3$, the fitting is less successful as one can conclude from Fig.1 and there does not exist only one region below the transition temperature, T_P. where the fit could be applied. The constant A extracted is of the order of 10 mV and is comparable to the one in semiconductors and, therefore, it seems reasonable to assume that the first term in (1)

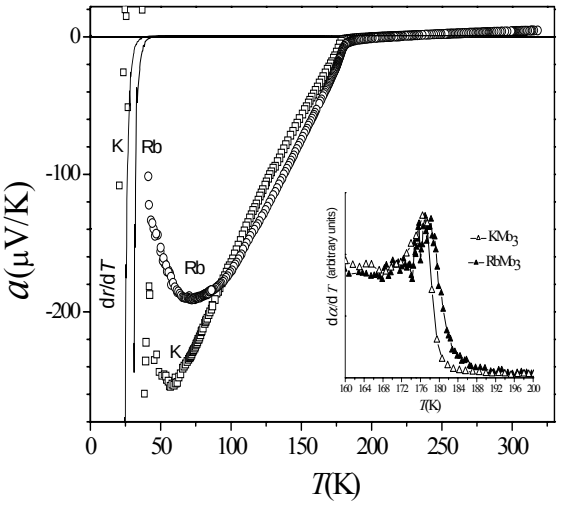

Figure 1. Thermopower of $Rb_{0.3}MoO_3$ (circles) and $K_{0.3}MoO_3$ (squares). The lines represent the derivative of resistivities in arbitrary units. Inset: The derivative of resistivities at the transition temperature.

arises from a real physical origin – the phonon drag origin. Some characteristics of the phonon drag thermopower, α_g, can explain expression:

$$\alpha_g = C_p/3ne \qquad (2)$$

where C_p is lattice specific heat and n is number of current carriers. As the Rb atom is larger then the K atom, it gives more electrons in a band although both of them are monovalent ones. In that case, the relation (2) explains why the extreme of $Rb_{0.3}MoO_3$ is lower than the extreme of $K_{0.3}MoO_3$. However, in the other hand, the temperature of the phonon drag extreme, T_g, is proportional the Debye temperature θ, and θ is proportional to sound velocity, which is inversely proportional to square root of mass. The molar mass of $Rb_{0.3}MoO_3$ is larger then the one of $K_{0.3}MoO_3$ and one expects T_g is lower for $Rb_{0.3}MoO_3$. However, the experiment does not show this expectation.

The existence of the linear term in (1), assumed as a diffusion thermopower, is even less clear. Due to the large extracted value of B, there are opinions that the relation (1) is not a proper function to reveal the underlying physics in similar compounds. We think that it is not a problem because the charge carriers are not constraint with Fermi-Dirac distributions which is responsible for the small thermopower in metals. But, the different signs of A and B indicates two kinds of carriers, and it is not clear, to us, why the phonon drag would act on only one kind of carriers unless this contribution from the holes can be neglected according to relation (2).

In Fig.1, we add the derivatives of resistivity of both compounds. These lines indicate why one cannot measure the thermopower below certain temperature. A detailed discussion will be given elsewhere [7].

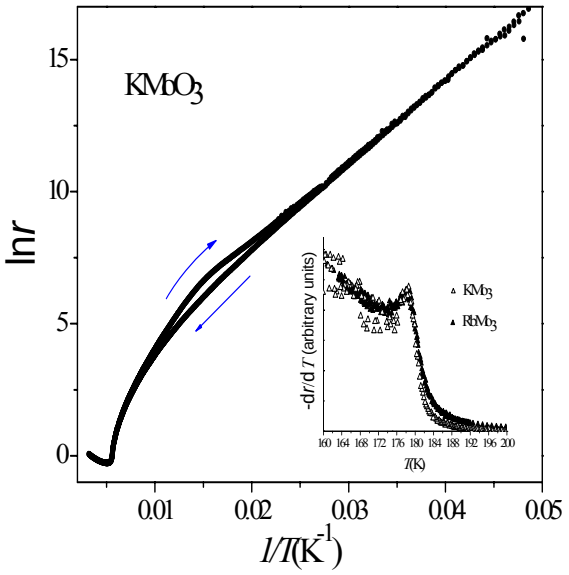

Figure 2. Resistivity $K_{0.3}MoO_3$ (squares). The lines represent the derivative of resistivity in arbitrary units of both compounds. Inset: The derivative of resistivities at the transition temperature.

The resistivity of $K_{0.3}MoO_3$ is presented in Fig.2 (a very similar result of the resistivity of $Rb_{0.3}MoO_3$ is omitted for clarity and will be given elsewhere [7]). First, one can notice a hysteretic behaviour just around where there is extreme in the thermopower. The highest difference between “up and down” resistivities is at 66 K and the extreme in the thermopower is at 57 K. In $Rb_{0.3}MoO_3$, the difference of the corresponding temperatures is even smaller and these temperatures are 76 K and 72 K, respectively. Also, there is certain and interesting hysteretic behaviuor noticed in the thermopower data, especially in $Rb_{0.3}MoO_3$ [7]. Interestingly enough, the resistivity shows activation behaviour below this region where the thermopower turns to zero but where it cannot be measured. Our results indicate that the thermopowers change the sign before it definitely reaches zero at 0 K. This part in thermopower indicates an abrupt change in the concentration of current carrier – perhaps a certain friezing of electrons.

Finally, we conclude that below T_p down to something below the thermopower minimum the concentration of current carrier changes and, therefore, the thermopower does not show pure $1/T$ behaviour and the position of the extreme is not where the theory predicts. Also, the resistivity in that regime does not show the expected activation behaviour.

In the insets of Figs 1 and 2, we show by the derivative the behaviour of the thermopowers and resistivities of the investigated systems around the transition temperature. First, one can notice that the transitions are rather clear and sharp. Therefore, we conclude that the samples are rather pure because very small number of impurities smears the transition considerably [2]. If one takes the highest point to represent T_p one obtains that T_P is 177.5 K for $K_{0.3}MnO_3$ 177.8 K for $Rb_{0.3}MnO_3$, i.e. the same value within the errors of the measurements. Therefore, the transition temperature depends mainly only on the structure of the MoO_6 ochtahedra.

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