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Possible Superconductivity in $TiSe_2$ Intercalated by Transition Metals

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Electric conductivity and magnetoresistence data for $TiSe_2$ intercalated by Fe^{2+} and Cr^{3+} are interpreted as superconducting state with $T_c \sim 5$ and 4 K, respectively.

KEY WORDS: superconductivity; intercalation compounds.

Intercalation of layered titanium dichalcogenides by silver and transition metals leads to decrease in the concentration of free charge carriers [1], lattice compression along normal direction to basal plane [2], growth of Ti oxidation state [3]. Such a behavior cannot be explained using the rigid band model, usually applied for interclation compounds. These properties were interpreted as a result of appearance of covalent centers Ti–M–Ti, forming upon intercalation due to hybridization of $Ti3d_z2$ states of the host lattice and valent states of intercalated metal [4]. These centers act as traps for free electrons, while the change of the lattice dimensions at intercalation was well described as a result of substitution of Ti–M–Ti with Ti–V–Ti (V-vacancy) centers [2]. As lattice deformation and degree of localization of charge carriers at formation of the Ti–M–Ti centers are in linear relation, so these centers may be considered as small polarons.

As polaron type of charge carriers is supposed to be important for properties of high temperature superconductors (see, for example, [5]), comparison of electrical properties of intercalation compounds with polaron charge carriers at cooling and HTSC cuprates is interesting. For this, we chose Cr_xTiSe_2 and Fe_xTiSe_2 systems, which demonstrate relatively moderate degree of localization, caused by moderate polaron shift value [2]. Magnetic moment of intercalated impurity has a specific interest; both these systems have antiferromagnetic type of interaction between intercalated atoms, Neel temperature is determined by impurity content [6, 7].

Single crystals, grown by gas transport method [3], had the following size: 7 × 5 × 0.1 mm^3 for Fe_xTiSe_2 and 6 × 5 × 0.05 mm^3 for Cr_xTiSe_2. Intercalant content was estimated using concentration dependence of unit cell parameters in *c*-direction, obtained earlier for powder samples: $Cr_{0.33}TiSe_2$ and $Fe_{0.5}TiSe_2$. Electrical conductivity was measured by standard 4-probe technique in temperature range 1.7–300 K and magnetic field $B = 0$–12 T, Center for Magnetic Measurements of Institute of Metal Physics UrD RAS.

Relative electrical resistivity for $Fe_{0.5}TiSe_2$ is shown in Fig. 1. The anomaly near ∼100 K coincides with Neel temperature for the same composition [6] and confirms determined iron content. Rapid drop of resistivity is visible below ∼5 K for $Fe_{0.5}TiSe_2$ and ∼4 K for $Cr_{0.33}TiSe_2$ (Fig. 2). At the point of the drop the slope of $R/R_{300}(T)$ increases 60 times (Fig. 1). Observed feature looks similar with transition to superconducting state. Magnetoresistivity $\rho(B)$ for both systems is shown in Fig. 3. This value increases as B increase and demonstrates a kink at some critical magnetic field 0.46 T for $Fe_{0.5}TiSe_2$ and 0.40 T for $Cr_{0.33}TiSe_2$ which we attribute with suppression of superconductivity. At higher magnetic field up to 12 T for $Fe_{0.5}TiSe_2$ $\rho(B)$ remains linear (Fig. 4).

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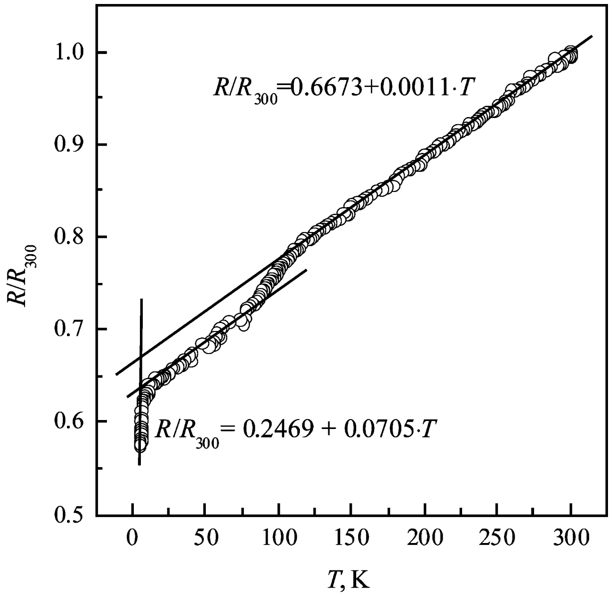
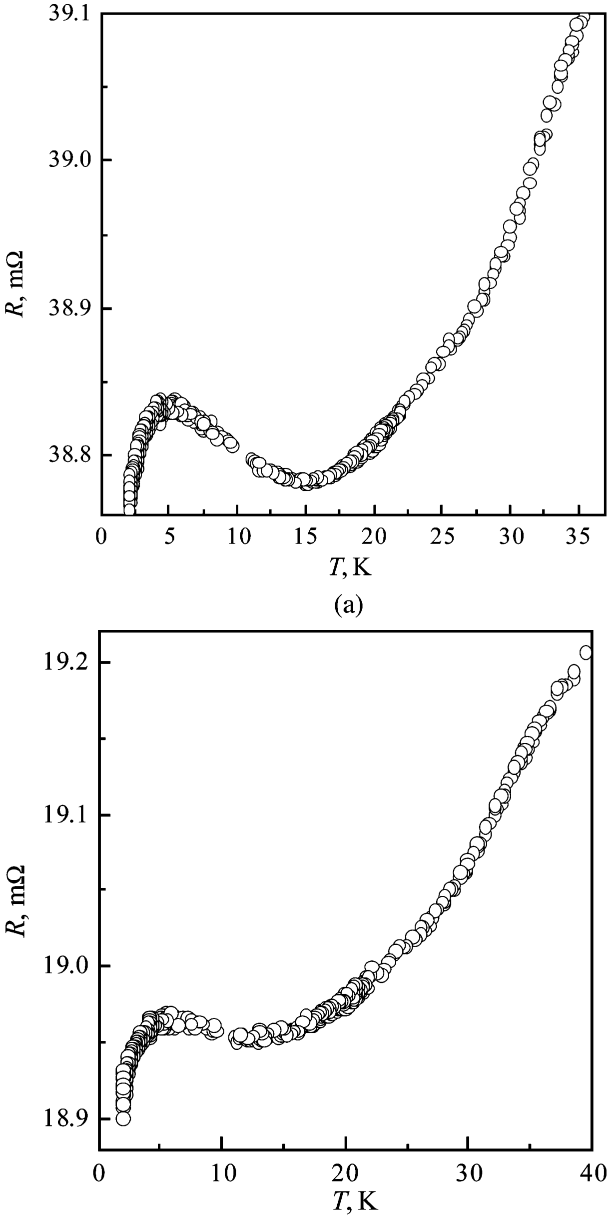


Fig. 1. Relative electrical resistivity for $Fe_{0.5}TiSe_2$.

Unfortunately, we did not have the possibility to decrease the temperature below 1.7 K and thus, were not able to observe the transition in whole. The observed effect is small, moreover, linear extrapolation of $R(T)$ in "superconducting" state (Fig. 1) gives a positive remnant resistivity at $T = 0$. It may be explained as inhomogeneous state of the material, when superconducting fractions are alternated by normal metal. Another explanation is the small concentration of Cuper pairs. Temperature dependences of electrical resistivity do not show any anomaly, which may be attributed with phase separation. Moreover, the phase transition of first order has kinetic barrier at low temperature because of low diffuse mobility of the components. So the first explanation seems less probable.



(a)

(b)

Fig. 2. Electrical resistivity for $Fe_{0.5}TiSe_2$ (a) and $Cr_{0.33}TiSe_2$ (b). Drop of resistivity below ~5 K for $Fe_{0.5}TiSe_2$ and ~4 K for $Cr_{0.33}TiSe_2$ we connect with superconducting state.

Small Cuper pair concentration may have the following reason. As it was predicted from band calculations, the hybrid state band $Ti3d_z2/M3d$ for M = Cr, Fe should have spin splitting [8]. For Cr_xTiSe_2 such a splitting was experimentally observed [3]. Evidently, when the splitting becomes significant it is possible to observe the gap between spin sub-bands. Observed activation type of electrical conductivity for $Cr_{0.33}TiSe_2$ [3] corresponds to this situation. For Cr^{3+} $x = 0.33$ concentration corresponds to transfer of one electron per unit cell, or by other words, exactly half filling of the hybrid state band. For Fe^{2+}-intercalated compound, the same situation will be obtained at x=0.5. The investigated single crystals had exactly these compositions what makes superconductivity impossible. In real crystals small amount of defects is possible, enough to form small quantity of Cuper pairs. These defects must have some excess of metal in comparison with stoichiometric composition (when

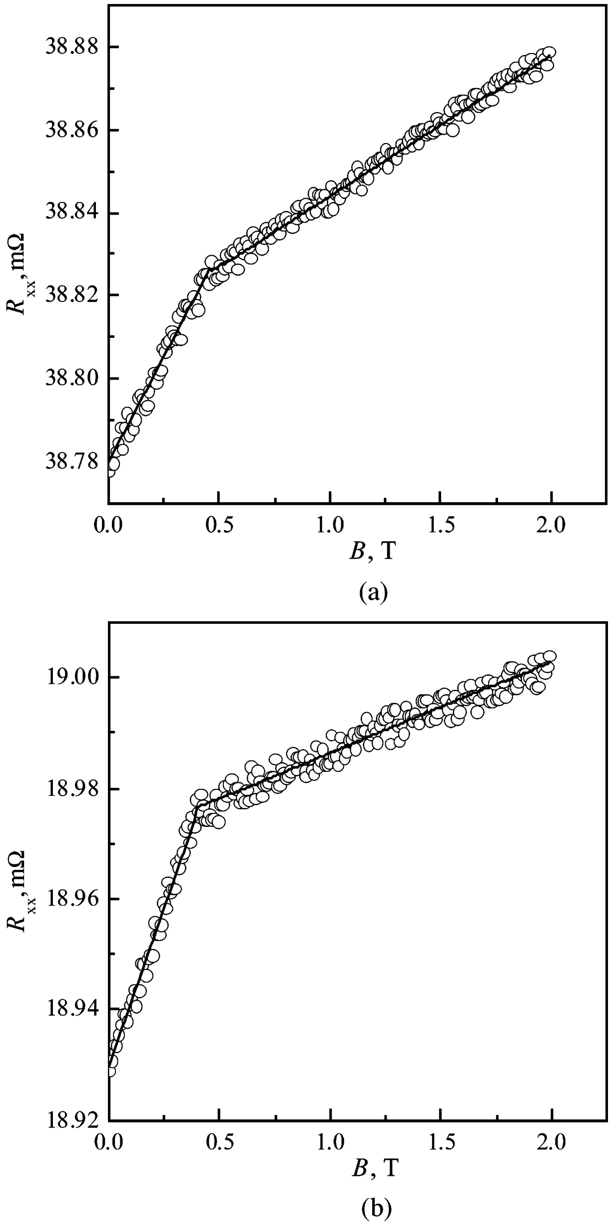


Fig. 3. Electrical resistivity for $Fe_{0.5}TiSe_2$ (a) and $Cr_{0.33}TiSe_2$ (b) as a function of external magnetic field. The kink at $B = 0.46$ T for $Fe_{0.5}TiSe_2$ and $B = 0.40$ T for $Cr_{0.33}TiSe_2$ we connect with suppress of superconductivity.

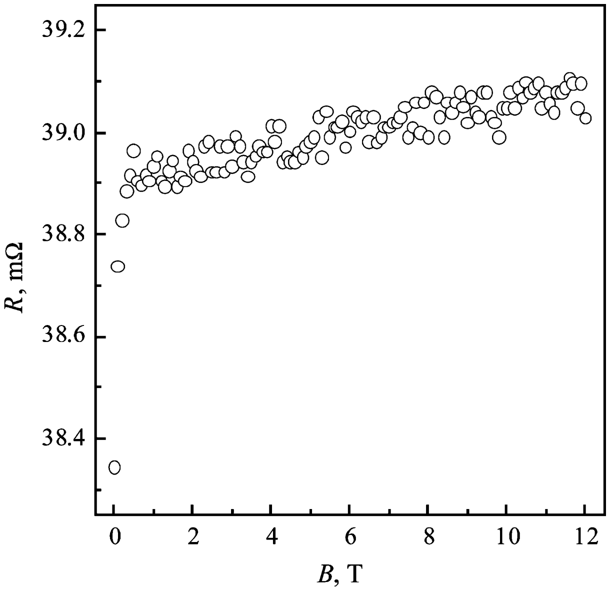


Fig. 4. Electrical resistivity of $Fe_{0.5}TiSe_2$ as a function of external magnetic field. The linear behavior remains up to 12 T.

the Fermi level is located into low spin sub-band, all electrons have the same spin and Cuper pairs can not be formed). This supposition may explain an absence of Meissner effect for powder $Cr_{0.5}TiSe_2$ [7], where the samples with precise stoichiometric composition were studied. With an aim to check this supposition, the measurement of temperature dependence of electric conductivity for powder sample with $Fe_{0.5}TiSe_2$ precise stoichiometric composition was done. The method of sample preparation and measurement was the same as for Cr_xTiSe_2 [3]. The data, shown in Fig. 5, demonstrate activation type

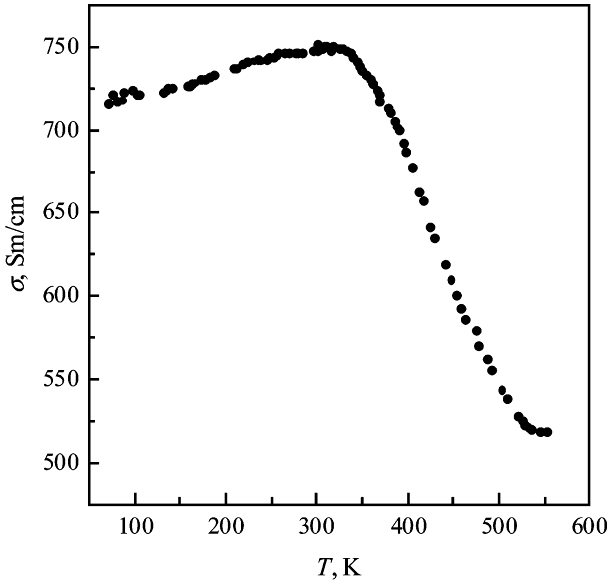


Fig. 5. Temperature dependence of electrical resistivity for powder sample with $Fe_{0.5}TiSe_2$ precise composition. Activation type of low temperature part of this function shows the closeness of Fermi level to energy gap.

of electric conductivity, in agreement with above supposition.

The relation between over-stoichiometric defects and superconducting state remains unclear and requests following investigation.

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