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Localization of charge carriers in materials with high polaron concentration

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Abstract

The influence of polaron concentration on the type of transition from band to activate conductivity has been investigated. For a single polaron in the crystal lattice or for material with polaron concentration higher than the percolation threshold, such a transition is continuous, in accordance with theory. However, for intermediate cases this process becomes step-like, because the rapid increase of density of states at Fermi level leads to a change of polaron characteristics. These suppositions are illustrated by experimental results (XPS-spectra, crystal structure analysis, DC conductivity) for intercalation compounds based on titanium dichalcogenides.

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The temperature dependence of the mobility of small polarons is non-monotonic. At both low and high temperature, the movement of polarons is band-like, whereas at intermediate temperatures, it is activated. This change has a continuous character [1] according to calculations based on a single particle approximation (SPA), which is correct for a small concentration of polarons. Intercalation of TiX_2 , $\text{X}=\text{Se}, \text{Te}$, by transition metals and silver results in the formation of covalent centres Ti-M-Ti, where M is the inserted metal. The formation of these centres leads to compression of the unit cell in the c -direction and electron localization on these centres in the form of small polarons [2]. The lattice deformation is

proportional to reduction of conductivity [2], to deviation of magnetic moment from spin value [3] and is determined by potential of ionization of inserted ion [4]. Electrons, localized at Ti-M-Ti centres, participate in charge transport with temperature dependence of conductivity typical for small polarons [5]. For these materials, the concentration of inserted metal and therefore, of polarons, may be varied over a wide range. This fact has allowed us to investigate the limit where the SPA justified.

We have experimentally investigated the crystal structure, DC conductivity, and XPS-spectra for M_xTiX_x , $\text{M}=\text{Ag}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}$, as a function of intercalated metal concentration. The method of sample preparation is described in Ref. [3]. In Fig. 1, the change of DC electrical conductivity as a function of sample quenching temperature for Fe_xTiSe_2 at 77 K is shown. A quench from

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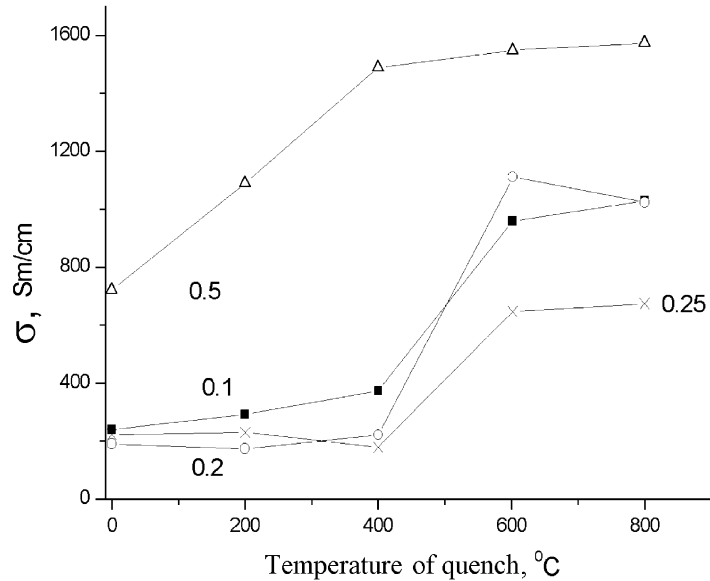


Fig. 1. The DC electrical conductivity of Fe_xTiSe_2 as a function of sample quenching temperature at 77 K.

$T > 500^\circ\text{C}$ fixes the state where the polarons are thermally delocalized. We see that for $0 < x \leq 0.25$, the transition from the high conductivity to the low conductivity regime is step-like, while for $x = 0.5$ (percolation threshold (PT) for the Fe sublattice [6,7]), the transition is continuous. Similar results are typical for M_xTiSe_2 . For $0 < x \leq 0.25$, localization of polarons leads to an increase of the density of states at the Fermi level and thereby, provides an increase of the dielectric constant. It results in a change of polaron characteristic and, as a consequence, the step-like character of the transition. For $x > 0.5$, an overlap of M3d-orbitals makes the density of states at the Fermi level only weakly dependent on polaron localization, and the SPA leads to the correct result.

Increase of the width of the conduction band when the concentration of impurity exceeds the PT may be observed experimentally as broadening of the XPS-spectral lines (Perkin-Elmer spectrometer, $\Delta E \sim 0.4\text{ eV}$), Fig. 2. Splitting of the Cr2p line of $\text{Cr}_{0.25}\text{TiSe}_2$ single crystals at the binding energy 574 eV is caused by an exchange interaction between Cr2p core hole and valence electrons when the last ones are spin polarized [3]. Broadening of the spin polarized sub-bands at $x > 0.25$

eliminates this splitting. The value $x = 0.25$ corresponds to the PT for Ti-M-Ti centres, unlike $x = 0.5$ which is the PT for the M sublattice [3]. Broadening of the hybrid Ti-M states leads to a decrease of the lifetime of the polarons. The concentration dependence of the unit cell lattice constant in the c -direction confirms these results [8]. For $x < 0.25$, an increase of x results in a linear increase of the quantity of centres of lattice compression (polarons) and causes a decrease of the c lattice parameter. At $x > 0.25$ (the PT for Ti-M-Ti centres), $c(x)$ increases due to the decrease of the polaron concentration.

From the experimental results considered, we can conclude that the SPA for polaron mobility gives the correct description of the temperature and concentration dependence of polaron properties when the density of states at Fermi level is not dependent on temperature. It corresponds to a polaron concentration either less than the Mott limit for a metal-insulator transition [1] (the conduction band is narrow throughout the entire temperature range) or more than the concentration providing direct overlap of orbitals in the impurity sublattice (the PT for the M atoms). For the last case, the conduction band is wide

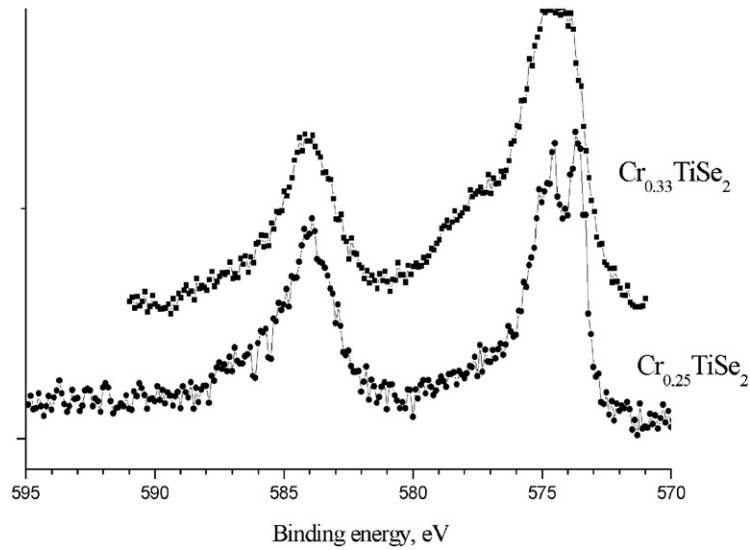


Fig. 2. X-ray photoemission spectra of Cr2p-states for $\text{Cr}_{0.25}\text{TiSe}_2$ and $\text{Cr}_{0.33}\text{TiSe}_2$.

throughout the entire temperature range and is not sensitive to polaron localization. Maximal temperature sensitivity of the density of states at the Fermi level occurs for impurity concentration equal to the PT in the polaron subsystem.

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