
**METALS
AND SUPERCONDUCTORS**

Structure and Physical Properties of Titanium Diselenide Intercalated with Nickel

V. G. Pleschev¹, N. V. Toporova¹, A. N. Titov², and N. V. Baranov^{1,2}

¹ Ural State University, pr. Lenina 51, Yekaterinburg, 620083 Russia

e-mail: valery.pleschov@usu.ru, nadya.toporova@usu.ru

² Institute of Metal Physics, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 18, Yekaterinburg, 620219 Russia

Received November 5, 2003

Abstract—The structure, electrical resistivity, thermopower, and magnetic susceptibility of titanium diselenide intercalated with nickel (Ni_xTiSe_2) are studied systematically in the nickel concentration range $x = 0–0.5$. In accordance with a model proposed earlier, strong hybridization of the $Ni3d/Ti3d$ states is observed, giving rise to suppression of the magnetic moment because of delocalization of the nickel d electrons. It is shown that the strain caused by the $Ni3d/Ti3d$ hybridization does not change the local coordination of a titanium atom. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

It was shown in [1, 2] that intercalation of titanium diselenide with transition and noble metals brings about the formation of an impurity band of hybridized $M3d/Ti3d$ states (M is an intercalated metal). This situation differs radically from the well-studied case of intercalation with alkali metals, where the electrons introduced with an intercalant remain free (metal with a variable Fermi level) [3, 4]. It has been established that this difference is due to the difference in the ionization potential of intercalated impurities. Hybridization of the valence states of an impurity with the $3d$ states of titanium occurs in all cases; however, if the ionization potential of an impurity is lower than a critical value, the hybridized states are significantly higher than the Fermi level and have no effect on the properties of the material [5]. If the ionization potential of an impurity exceeds the critical value, the crystal lattice undergoes compression along the normal to the plane of basal $TiSe_2$ layers [5], the density of free charge carriers decreases or vanishes [1], the magnetic moment of the impurity is suppressed [6], etc. These experimental observations can be explained in terms of $Ti–M–Ti$ covalent centers, which act as free-electron traps and cause deformation of the host lattice [5]. It has been found that the degree of localization of conduction electrons on these centers and the degree of lattice deformation are proportional to each other and determined by the position of the impurity band with respect to the Fermi level [1].

The Ni_xTiSe_2 system was first synthesized in the 1970s [7]. The concentration dependences of the unit cell parameters presented in [7] show that the compression strain along the normal to the $TiSe_2$ layer plane is the highest among all transition-metal compounds studied to date. Therefore, one might expect that this mate-

rial will exhibit all properties characteristic of intercalation compounds with an impurity band lying below the Fermi level. However, the electrical and magnetic properties of Ni_xTiSe_2 and its fine structural features (the Ni atom position, the effect of intercalation on the positions of host atoms, etc.) remain poorly studied. In this work, we performed a detailed study of the atomic structure, resistivity, thermopower, and magnetic susceptibility of Ni_xTiSe_2 .

2. EXPERIMENTAL

Ni_xTiSe_2 samples ($0 < x < 0.5$) were obtained from the following elements using the conventional method of synthesis in an ampoule: titanium (purified by iodide distillation) of 99.99% purity (Aldrich 30.581-2), OSCh-19-5-grade selenium of 99.999% purity, and electrolytic nickel of 99.95% purity. First, titanium diselenide was sintered at 900°C over one week. Then, the material obtained was ground and, after mixing with the corresponding amount of powdered nickel, was pressed and again annealed at 800°C over one week. The sintering temperature was taken lower than the temperature of synthesis of the host compound in order to prevent the substitution of nickel for titanium. Since the material obtained after this annealing was inhomogeneous, it was again ground, pressed, and subjected to annealing. After this procedure, the material generally became sufficiently homogeneous. In [7], it was shown that several different superstructures can form in the material; however, the thermal history of the samples was not detailed. In order to prevent the influence of the ordering of nickel on the physical properties of the material, the samples were quenched from the temperature of the last homogenizing annealing (800°C).

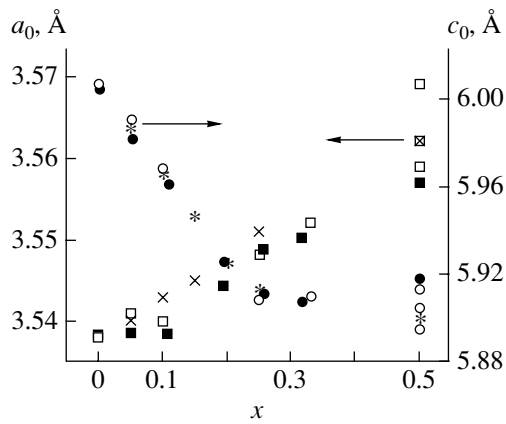


Fig. 1. Concentration dependences of the unit cell parameters a_0 and c_0 of Ni_xTiSe_2 . Filled symbols are data from this work, and open symbols, crosses, and asterisks are data from [7], where the results obtained at two different laboratories are summarized. (The differences between the results are due to the different preparation conditions of the samples.)

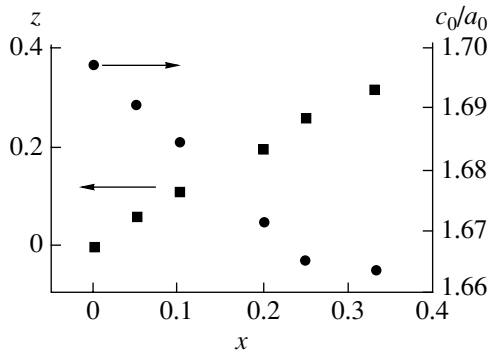


Fig. 2. Dependences of the ratio c_0/a_0 and the coordinate z of the Se atom along the c axis on the nickel concentration.

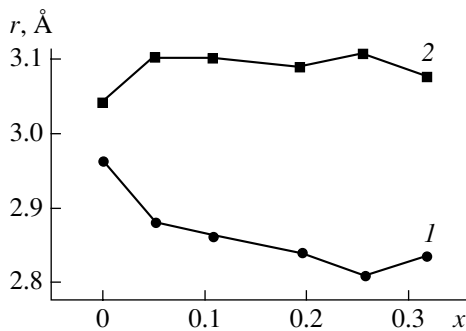


Fig. 3. Dependences of (1) the van der Waals gap width and (2) the Se-Ti-Se layer width on the nickel content in Ni_xTiSe_2 .

X-ray diffraction studies were performed on powder samples using a DRON-4-13 diffractometer (plane graphite monochromator, $\text{CoK}\alpha$ radiation, step 0.01° ,

angle range 14° – 80°). The structural characteristics of Ni_xTiSe_2 were calculated using the method of full-profile refinement of x-ray diffraction patterns (the GSAS software package [8]). The lattice parameters calculated by us agree with the available literature data [7], which indicates the high quality of the material studied by us. The magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design, USA). The resistivity was measured on pressed samples using the conventional four-probe method.

3. RESULTS AND DISCUSSION

The results of full-profile refinement show that the material has the same structure (CdI_2) and belongs to the same space group ($P\bar{3}m1$) as the original host lattice up to the intercalant content $x = 0.33$ without nickel ordering. The coordinates of the unit cell basis are Ti (0, 0, 0), Se ($1/3$, $2/3$, z), and Ni (0, 0, $1/2$). The best fit to the experimental data is obtained in the case where the intercalated Ni atoms are assumed to be in the octahedral positions in the van der Waals gap.

As seen from Fig. 1, nickel intercalation decreases the lattice parameter along the normal to the basal plane (c_0) up to the intercalant concentration $x = 0.25$. This behavior is typical of titanium chalcogenides intercalated with transition metals [1] and is commonly explained by the formation of covalent Ti-Ni-Ti bridges, which pull the host lattice layers closer together. These centers also act as free-carrier traps and can be considered covalent polarons [9]. ARPES studies of the analogous $\text{Ni}_{1/3}\text{TiSe}_2$ system have shown that the formation of such centers is accompanied by the appearance of a dispersionless band approximately 1 eV below the Fermi level [10]. According to [11], an impurity polaron band has similar properties. Since this band is oriented along the M - Γ direction in the Brillouin zone, it was concluded in [10] that this band is formed by the $\text{Ni}3d_{zz}/\text{Ti}3d_{zz}$ hybridized states.

As shown in [5], the amount of strain caused by the formation of the centers mentioned above is determined (for a given host lattice) by the ionization potential of the intercalant. The dimension of the deformed Ti-Ni-Ti cluster along the normal to the basal plane as calculated from the $c_0(x)$ dependence is characterized by the lattice parameter $c_0 = 5.631$ Å, which is close to the value $c_0 = 5.611$ Å calculated in [5] from the ionization potential of the Ni^{2+} ion. This discrepancy can be due to the screening effect not being fully taken into account.

The significant changes in the lattice parameters of TiSe_2 caused by nickel intercalation (a decrease in c_0 and a simultaneous increase in a_0) lead to a change in the ratio c_0/a_0 , which characterizes the distortion of the chalcogen octahedron surrounding a titanium atom [12] (Fig. 2). From the concentration dependences of the Se-Ti-Se layer thickness r_L and the van der Waals gap width r_G shown in Fig. 3, it follows, however, that the

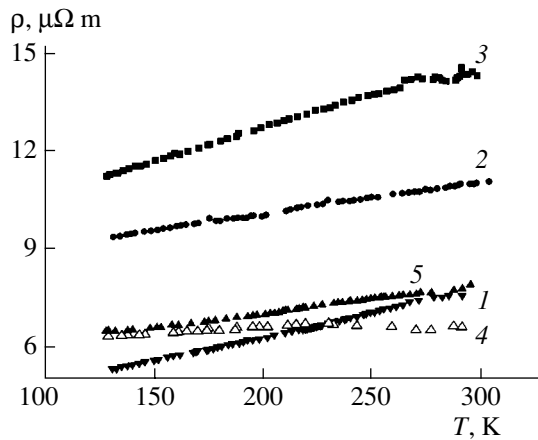


Fig. 4. Temperature dependences of the resistivity of Ni_xTiSe_2 for different values of x : (1) 0.1, (2) 0.2, (3) 0.25, (4) 0.33, and (5) 0.5.

lattice deformation along the normal to the basal plane is due solely to a decrease in the width of the van der Waals gap. If the deformation is of polaron nature, this behavior is quite natural and also indicates that the geometric characteristics of the local surrounding of a Ti atom remain unchanged. The latter fact is very important, because the shape of the chalcogen octahedron determines the mutual arrangement of the $\text{Ti}3d$ bands [13]. If the octahedron is regular in shape, the $\text{Ti}3d_{zz}$, $\text{Ti}3d_{yy}$, and $\text{Ti}3d_{xx-yy}$ orbitals forming the conduction band bottom are degenerate in energy. Extension of the octahedron along the c axis causes the $\text{Ti}3d_{zz}$ orbital to be lower in energy than the orbitals lying in the (x, y) plane, and compression of the octahedron along the c axis has the opposite effect. The decrease in c_0 and increase in a_0 suggest that the chalcogen octahedron is compressed along the c axis and that the $\text{Ti}3d_{zz}/\text{Ni}3d_{zz}$ hybridization becomes weaker, thereby causing polarons to disappear gradually. On the other hand, the constancy of the coordination of Se atoms to titanium indicates that the interaction between the Ti and Ni sublattices does not change in character over the entire concentration range studied. Therefore, an increase in the nickel content causes the polaron concentration to increase but does not change the polaron characteristics.

The conductivity of Ni_xTiSe_2 is close in magnitude to that observed in the original TiSe_2 but is different from that of other materials in which polarons form. The temperature dependence of resistivity is metallic in character for all compositions studied (Fig. 4); i.e., the mobility of charge carriers is fairly high. This result contradicts the conclusion (drawn from the x-ray data) that the conduction band is associated with polarons. For such strong deformation of the lattice, a much higher degree of localization of charge carriers could be expected. It is likely that the conduction band is formed not only by the d_{zz} orbital but also by other Ni orbitals

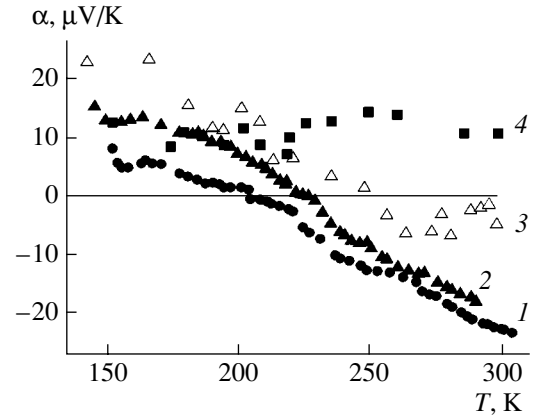


Fig. 5. Temperature dependences of the thermopower of Ni_xTiSe_2 for different values of x : (1) 0.2, (2) 0.25, (3) 0.33, and (4) 0.5.

hybridized with Ti and Se orbitals. In this case, the electrons are less localized and have a higher mobility.

As seen from Fig. 4, the resistivity is maximal for $\text{Ni}_{0.25}\text{TiSe}_2$. It should be noted that, in contrast to other intercalation compounds $M_x\text{TiSe}_2$ ($M = \text{Fe}, \text{Co}, \text{Cr}, \text{Mn}, \text{Ag}$), the conductivity does not increase with the intercalant content in the case of intercalation with nickel. Therefore, the effect of nickel on the conductivity reduces to a change in the mobility of carriers rather than in their density. As shown in [5], the composition with $x = 0.25$ corresponds to the percolation threshold over titanium atoms coordinated to the impurity (site percolation problem for a triangular lattice with nearest neighbor interaction). This result correlates with the discontinuity in slope observed in the concentration dependence of c_0 at nickel content $x = 0.25$ (Fig. 1). It is likely that at $x < 0.25$ the conductivity is associated with the sublattice of sites whose nearest environment does not contain nickel atoms, whereas at $x > 0.25$ it is associated with the sublattice of titanium atoms coordinated to nickel. The point $x = 0.25$ corresponds to the minimum connectivity of both sublattices.

For samples with different intercalant content, the thermopower changes sign as a function of temperature (Fig. 5), which indicates a changeover from p -type to n -type conductivity with heating. The temperature at which this changeover occurs increases monotonically with the nickel content. Therefore, an increase in the intercalant content causes a monotonic change in the ratio between the electron and hole densities, whereas the anomaly observed in the concentration dependence of conductivity is associated with their mobilities. The increase in the contribution from holes to charge transport with increasing intercalant concentration can be due to the increasing localization of electrons in the $\text{Ti}3d_{zz}/\text{Ni}3d$ hybridized band.

The magnetic susceptibility χ of Ni_xTiSe_2 (Fig. 6) is significantly lower than that of analogous compounds

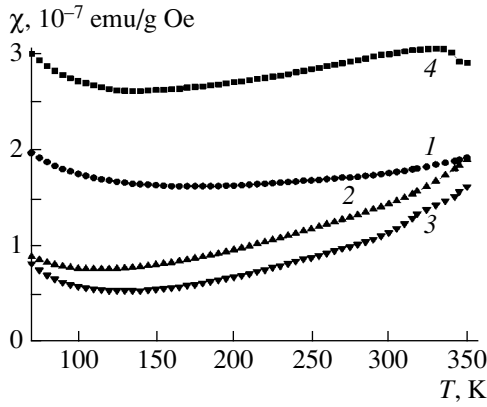


Fig. 6. Temperature dependences of the magnetic susceptibility of Ni_xTiSe_2 for different values of x : (1) 0.1, (2) 0.25, (3) 0.33, and (4) 0.5.

with Cr, Mn, Fe, and Co [14], and its temperature dependence is very weak and cannot be described by the commonly used expression

$$\chi = \chi_0 + \frac{C}{T - \Theta}, \quad (1)$$

where the first term (χ_0) is the temperature-independent diamagnetic contribution from the ionic cores and the Pauli paramagnetic contribution from the conduction electrons and the second term is the Curie–Weiss contribution from localized magnetic moments. Above 80 K, the magnetic susceptibility is observed to increase with heating. Since the Curie–Weiss contribution does not exhibit such behavior, the main contribution can be due only to the conduction electrons. The temperature dependence of this contribution to the magnetic susceptibility is described by [15]

$$\chi_P = \mu_B^2 g(E_F) \left[1 - \left\{ \left(\frac{g'}{g} \right)^2 - \left(\frac{g''}{g} \right) \right\}_{E=E_F} T^2 \right], \quad (2)$$

Table 1. Parameters for calculating the magnetic susceptibility from Eqs. (1) and (2)

Parameter	x			
	0.1	0.25	0.33	0.5
$\chi_0 \times 10^{-7}$, emu/g Oe	1.134	0.285	-0.2015	1.935
$C \times 10^{-6}$, emu K/g Oe	5.852	3.789	6.759	7.184
$P \times 10^{-12}$, emu/g Oe K ²	0.487	1.168	1.281	0.978
$\chi_P \times 10^{-7}$, emu/g Oe	6.134	5.285	4.799	6.935
μ_{eff}, μ_B	0.31	0.17	0.19	0.16

Note: $P = \mu_B^2 g(E_F) \left[\left\{ \left(\frac{g'}{g} \right)^2 - \left(\frac{g''}{g} \right) \right\}_{E=E_F} \right]$, $\chi_P = \chi_0 + \chi_D$,

$$\chi_D = -5 \times 10^{-7} \text{ emu/g Oe.}$$

where g , g' , and g'' are the density of states at the Fermi level and its first and second derivatives with respect to energy, respectively. However, numerical calculation showed that Eq. (2) likewise cannot describe the temperature dependence of χ . We succeeded in describing this dependence with the sum of Eqs. (1) and (2). The corresponding parameters are listed in Table 1. It is interesting that the effective Ni magnetic moments are small, which agrees with the available data for $x = 0.1$ and 0.2 [16]. Such suppression of the magnetic moment was also observed in the Co_xTiSe_2 and Cr_xTiSe_2 systems [6]. Among all analogous intercalated materials, Ni_xTiSe_2 undergoes the maximum compression along the c axis and, accordingly, shows the maximum difference between the experimentally observed magnetic moment and the magnetic moment of the free ion. Another specific feature is the large negative quadratic contribution, which comes either from the strong temperature dependence of the Fermi level position or from the strong energy dependence of the density of states at the Fermi level. This feature is observed over a wide concentration range; therefore, it is unlikely that the significant change in the electron density produced by the intercalant does not cause the Fermi level to leave the region of the strong energy dependence of the density of states. It follows that the quadratic contribution to the temperature dependence of χ is due to the strong temperature dependence of the Fermi level. Such a strong dependence is likely if the charge carriers are polarons. Indeed, a change in temperature causes a change in the carrier polarization in this case, thereby varying the density of states at the Fermi level and the position of the Fermi level [11].

It should be noted that $\text{Ni}_{0.5}\text{TiSe}_2$ differs in terms of its properties from other Ni_xTiSe_2 compounds. In contrast to compositions with $x < 0.5$, this compound belongs to the monoclinic crystal system and is characterized by the $I2/m$ space group, $Z = 4$, and the divergence factor $R_w = 6\%$ (Table 2), which is the result of the $\sqrt{3}a_0 \times a_0 \times 2c_0$ ordering of nickel in van der Waals gaps. The nickel content $x = 0.5$ corresponds to the percolation threshold in the impurity sublattice. This circumstance, as well as the pure topological ordering of the impurity in the van der Waals gaps, can be the reason for the monoclinic distortions. The change in the symmetry of the unit cell causes an increase in the magnetic susceptibility and conductivity, but the conductivity remains p -type in the entire temperature range covered. This conclusion is supported by the fact that the thermopower does not change sign as the nickel content reaches $x = 0.5$ and that the magnetic susceptibility is virtually independent of temperature.

Thus, the coincidence of the percolation threshold in the sublattice of titanium atoms coordinated to nickel with the position of the anomaly in the concentration dependences of the resistivity and lattice parameters and the coincidence of the nickel ordering point with the percolation threshold in the impurity atom sublattice

Table 2. Structural parameters of the $\text{Ni}_{0.5}\text{TiSe}_2$ compound

	$\text{Ni}_{0.5}\text{TiSe}_2$ ($\text{CuK}\alpha$)		x	y	z	$U, \text{\AA}^2$
$a_0, \text{\AA}$	6.161 (1)	Ni ($2/m$)	0	0	0	0.12 (1)
$b_0, \text{\AA}$	3.567 (1)	Ti (m)	0.0092 (2)	0	0.2504 (4)	0.05 (2)
$c_0, \text{\AA}$	11.836 (2)	Se1 (m)	0.1643 (6)	1/2	-0.1218 (2)	0.07 (5)
β, deg	90.293 (3)	Se2 (m)	0.3322 (6)	0	0.1184 (1)	0.02 (3)

Note: Thermal parameters U are calculated in the isotropic approximation.

tice suggest that the charge carriers are localized. This conclusion correlates well with the observed suppression of the nickel magnetic moment. However, the carrier localization appears to be significantly different in character from that observed in titanium diselenide intercalated with other transition metals. This difference is likely due to the fact that the hybridized states in which the conduction electrons are localized involve many $\text{Ni}3d$ orbitals.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project nos. 01-03-32620, 01-03-96502) and the federal program "Universities of Russia" (project no. UR.01.01.005).

REFERENCES

1. A. Titov, S. Titova, M. Neumann, V. Pleschev, Yu. Yarmoshenko, L. Krasavin, A. Dolgoshein, and A. Kuranov, *Mol. Cryst. Liq. Cryst.* **311**, 161 (1998).
2. A. A. Titov and A. V. Dolgoshein, *Fiz. Tverd. Tela* (St. Petersburg) **40** (7), 1187 (1998) [*Phys. Solid State* **40**, 1081 (1998)].
3. P. C. Klipstein, C. M. Pereira, and R. H. Friend, *Philos. Mag. B* **56** (5), 531 (1987).
4. P. C. Klipstein and R. H. Friend, *J. Phys. C: Solid State Phys.* **20** (26), 4169 (1987).
5. A. A. Titov, A. V. Dolgoshein, I. K. Bdikin, and S. G. Titova, *Fiz. Tverd. Tela* (St. Petersburg) **42** (9), 1567 (2000) [*Phys. Solid State* **42**, 1610 (2000)].
6. A. M. Titov, A. V. Kuranov, V. G. Pleschev, Yu. M. Yarmoshenko, M. V. Yablonskikh, A. V. Postnikov, S. Plogmann, M. Neumann, A. V. Ezhov, and E. Z. Kurmaev, *Phys. Rev. B* **63**, 035 106 (2001).
7. Y. Arnaud, M. Chevreton, A. Ahouanjiou, M. Danot, and J. Rouxel, *J. Solid State Chem.* **18**, 9 (1976).
8. A. C. Larson and R. B. von Dreele, *LANSCE.MS-H805* (Los Alamos National Laboratory, Los Alamos, 1986), NM 87545.
9. N. F. Mott and E. A. Davis, *Electron Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979; Mir, Moscow, 1982).
10. T. Matsushita, S. Suga, and A. Kimura, *Phys. Rev. B* **60** (3), 1678 (1999).
11. A. S. Alexandrov and N. Mott, *Polarons and Bipolarons* (World Sci., Singapore, 1995).
12. T. Hibma, *Structural Aspects of Monovalent Cation Intercalates of Layered Dichalcogenides* (Academic, London, 1982), p. 285.
13. W. V. Liang, in *Proceedings of the NATO Advanced Study Institute Physics and Chemistry of Electrons and Ions in Condensed Matter, Cambridge, UK* (Reidel, Dordrecht, 1984), p. 459.
14. A. V. Kuranov, V. G. Pleschev, A. N. Titov, N. V. Baranov, and L. S. Krasavin, *Fiz. Tverd. Tela* (St. Petersburg) **42** (11), 2029 (2000) [*Phys. Solid State* **42**, 2089 (2000)].
15. S. V. Vonsovskii, *Magnetism* (Nauka, Moscow, 1971; Wiley, New York, 1974).
16. Y. Tazuke and T. Takeyama, *J. Phys. Soc. Jpn.* **66** (3), 827 (1997).

Translated by Yu. Epifanov