
**MAGNETISM
AND FERROELECTRICITY**

Hierarchy of Percolation Thresholds and the Mechanism for Reduction of Magnetic Moments of Transition Metals Intercalated into TiSe₂

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Abstract—The concentration dependences of the effective magnetic moment of transition metal atoms intercalated into TiSe₂ are analyzed in the framework of the percolation theory. It is shown that, depending on the degree of localization of impurity states, the effective magnetic moment is determined by the overlap of 3d orbitals of transition metals or orbitals of titanium atoms coordinated by impurity atoms. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Intercalated materials based on titanium dichalcogenides are formed through the intercalation of atoms of different metals into the interlayer space of the host lattice. Earlier investigations [1–4] revealed that the intercalation of transition metals and silver into TiSe₂ brings about the formation of Ti–Me–Ti covalent centers, where Me is an intercalated metal (Ti, Cr, Fe, Co, Ni, Ag). The formation of covalent centers can be judged from the distortion of the host lattice. In the case when impurity atoms are ionized with electron transfer to the conduction band of the initial compound, the lattice parameter c_0 increases with an increase in the impurity content x . At the same time, the formation of covalent centers is accompanied by a decrease in the lattice parameter c_0 with an increase in the impurity content x . Electrons transferred with intercalant atoms are localized at these centers. Such centers serve as traps of free charge carriers, on the one hand, and as strain centers of the lattice, on the other hand. Consequently, these centers can be treated as polarons. Upon the formation of polarons in the lattice, the influence of an intercalated impurity atom is localized in the vicinity of the site occupied by this atom. As a result, the dependences of the electrical and magnetic properties of intercalation materials on the intercalant content exhibit a pronounced nonmonotonic behavior. Therefore, the concentration dependences of the physical parameters of intercalation materials can be described in terms of the percolation theory.

Earlier [3–5], we demonstrated that, for TiSe₂-based intercalation compounds, the concentration depen-

dences of the kinetic properties and the host-lattice strain arising upon intercalation of transition metals are adequately described within the percolation theory. The characteristic concentrations are in close agreement with the percolation threshold analytically calculated by Sykes and Essam [6], who solved the site problem for a triangular lattice with sites occupied by intercalated atoms. However, the question as to which physical quantity plays the role of the percolation parameter remains open. In our opinion, it is reasonable to consider at least three possible mechanisms of percolation: (1) the overlap of lattice distortion fields in the vicinity of each intercalated atom, (2) the overlap of orbitals of impurity atoms, and (3) the overlap of orbitals of titanium atoms coordinated by impurity atoms (the overlap of orbitals of Ti–Me–Ti centers). At the same time, elucidation of the nature of the percolation thresholds is of considerable importance in interpreting the observed concentration dependence of the effective magnetic moment μ_{eff} of intercalated atoms. As was shown in our previous work [7], the difference between the effective magnetic moment μ_{eff} and the spin moment of a free ion is directly proportional to the lattice strain. The reduction of magnetic moments of impurity atoms can be explained in the framework of the Anderson impurity model for magnetic ions with an unfilled $d(f)$ shell [8]. According to this model, the magnetic moment of an atom is determined by the difference in the occupancies of spin-polarized $d(f)$ orbitals. The hybridization of the orbitals with the environment leads to their broadening and, hence, to a decrease in the difference between the occupancies of these orbitals, which, in turn, results in

a decrease in the magnetic moment. Consequently, the dominant role in the reduction of the magnetic moment is played by the concentration (temperature, etc.) dependence of the d subband of impurity atoms. However, it is clear that the hybridization is only one of the possible mechanisms of band broadening. This broadening can also be caused by the increase in the overlap of orbitals as the impurity atoms approach each other with an increase in their concentration. Therefore, the identification of percolation features with points of anomalies in the concentration dependence of the effective magnetic moment μ_{eff} will make it possible to reveal the mechanism responsible for the reduction of the magnetic moments of impurity atoms intercalated into titanium dichalcogenides.

Since the impurity atoms occupy octahedral positions forming a triangular lattice, the impurity concentration corresponding to the percolation threshold in the case of mechanism (2) is easily determined to be $x = 0.5$ [6] (where x is the dimensionless impurity concentration per unit cell containing only one octahedral position that can be occupied by an impurity atom). For mechanisms (1) and (3), the critical impurity concentration is equal to $x = 0.25$. This follows from the structural features of the materials under investigation. Actually, if an octahedral position in the structure of these materials is occupied, the octahedral positions nearest to this occupied position along the normal to the basal plane of the crystal cannot be occupied by impurity atoms [9]. Consequently, the intercalation of each impurity metal atom leads to the formation of a Ti– Me –Ti center with two titanium atoms coordinated by the impurity atom. Therefore, at the impurity concentration $x = 0.25$, the concentration of titanium atoms coordinated by impurity atoms coincides with the percolation threshold in the triangular lattice. Since the density of octahedral positions that cannot be occupied upon intercalation is equal to $2x$ (taking into account that each blocked position belongs to two unit cells), the impurity concentration corresponding to the critical value $x = 0.5$ also amounts to $x = 0.25$.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The concentration dependences of the lattice parameters will be discussed using the data obtained earlier in [2, 5, 9]. The effective magnetic moments of impurity atoms were determined from the temperature dependence of the magnetic susceptibility in the paramagnetic temperature range. The measurements were performed by the Faraday method according to the technique described in [4].

The x-ray photoelectron spectra of Cr_xTiSe_2 single crystals were recorded on a Perkin-Elmer spectrometer with an energy resolution of 0.4 eV. The spectra were excited with monochromated AlK_α radiation. Samples were applied on an adhesive conducting substrate. In

order to reduce undesirable effects of adsorbed atmospheric gases and carbon on the spectra, the sample surface was mechanically cleaned directly in the measuring chamber of the spectrometer under vacuum (at a residual pressure of 10^{-8} Torr).

Single-crystal samples were used to improve the resolution. On the one hand, this approach restricted detailed analysis of the influence of the impurity content on the electronic structure to the compositions with $x = 0.10$ and 0.33 for which we succeeded in growing the single crystals. On the other hand, the use of single-crystal samples with a juvenile surface, which was prepared by cleaving directly in the spectrometer chamber under high vacuum, made it possible to obtain conclusive results. The crystals were grown by the gas-transport reaction method with the use of I_2 as a gas carrier. The growth procedure was described in detail in [7].

3. RESULTS AND DISCUSSION

The concentration dependences of the lattice parameters for Me_xTiSe_2 ($Me = \text{Cr, Fe, Co, Ni}$) compounds exhibit anomalies in the form of kinks at $x = 0.25$. It is obvious that these anomalies can be associated with the percolation. However, the question as to whether mechanism (1) or mechanism (3) is dominant remains unclear. The contributions from the mechanisms of percolation due to the overlap of lattice distortion fields and the overlap of orbitals can be separated using different degrees of localization of Ti– Me hybrid orbitals for different metals. As was shown in our earlier work [5], the degree of localization is governed by the lattice strain arising upon intercalation of impurity atoms. It is clear that, if the localization is sufficiently strong, the percolation through mechanism (3) can be completely absent. This situation can occur when the spatial extension of the orbitals of titanium atoms coordinated by impurity atoms is less than half the distance between the nearest localization centers. In turn, this distance cannot be less than the lattice parameter a_0 . The strain reaches a maximum in Co_xTiSe_2 compounds. Hence, we can expect that, in these compounds, the percolation through mechanism (3) is absent. In this case, the anomaly at $x = 0.25$ should be assigned solely to the overlap of distortion fields. Indeed, an increase in the cobalt impurity content above the critical value $x = 0.25$ results only in a decrease in the slope of the concentration dependence of the lattice parameter $c_0(x)$ for Co_xTiSe_2 compounds. This can be explained by the interaction of strain centers due to the overlap of their distortion fields. Therefore, an increase in the cobalt impurity content $x > 0.25$ leads to an increase in the concentration of strain centers with a simultaneous decrease in the strain per intercalated atom. This inference is consistent with the data obtained in our work [4], in which we observed linear concentration dependences of the electrical conductivity and the Seebeck coefficient in the cobalt concentration range $x = 0–0.33$.

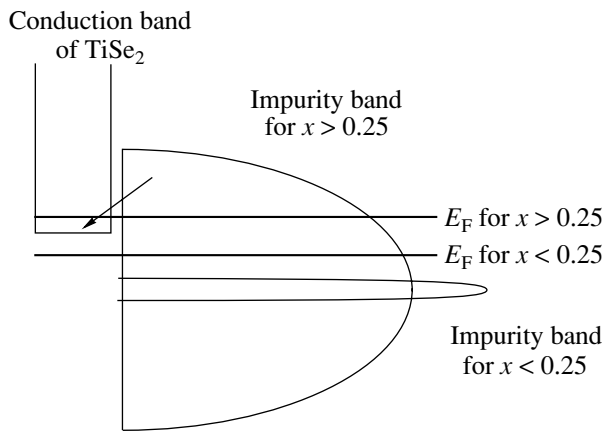


Fig. 1. A schematic diagram illustrating the shift of the Fermi level upon broadening of the impurity band due to the overlap of orbitals of localization centers. The arrow indicates the electron transfer from the polaron band to the conduction band of the host lattice with an increase in the energy at the top of the polaron band.

Consequently, the intercalation of each cobalt atom at a cobalt content below and above $x = 0.25$ does not change the localization of charge carriers.

The above dependence differs substantially from the concentration dependence of the lattice parameter $c_0(x)$ for Cr_xTiSe_2 compounds, in which the strain is minimum and, hence, the extension of orbitals of Ti–Cr–Ti centers is maximum. In these compounds, an increase in the chromium content $x > 0.25$ results in an increase in the lattice parameter c_0 [10]. Apparently, this difference should be caused by the additional contribution from the overlap of orbitals of Ti–Cr–Ti centers. An increase in the concentration of strain centers cannot be attended by a decrease in the total strain. Such a behavior can be explained solely by the decrease in the number of strain centers in the chromium concentration range $x > 0.25$. Physically, this situation can be interpreted as follows (Fig. 1): the impurity band can be broadened to an extent that the impurity band top appears to be higher than the conduction band bottom of TiSe_2 . As a consequence, electrons partially transfer to the conduction band of TiSe_2 . In the impurity band, the states between the impurity band top and the Fermi level turn out to be empty, which, in essence, corresponds to a partial decay of localization centers.

Thus, the overlap of distortion fields around intercalated impurity atoms results in a decrease in the strain induced upon intercalation. A decrease in the contraction of the lattice parameter c_0 can be provided only by an overlap of orbitals of localization centers. Relevant direct experimental evidence can be obtained by analyzing the electronic structure of the compounds under investigation in the chromium concentration ranges $x < 0.25$ and $x > 0.25$.

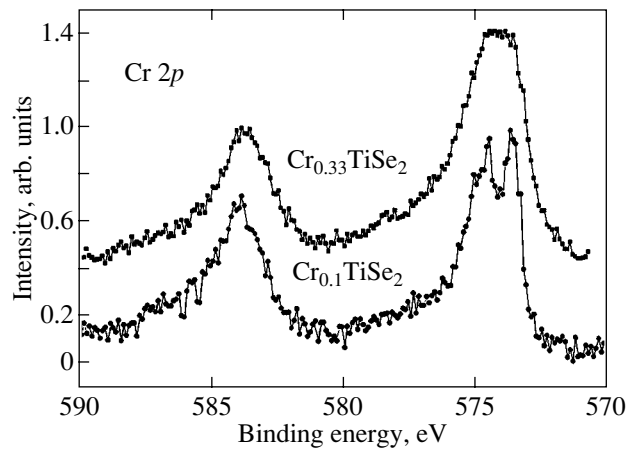


Fig. 2. Cr $2p$ photoemission spectra of Cr_xTiSe_2 compounds with intercalant concentrations below ($x = 0.1$) and above ($x = 0.33$) the percolation threshold in the sublattice of Ti–Cr–Ti centers. The splitting of the line at an energy of 574 eV (Cr $2p_{3/2}$) in the spectrum of $\text{Cr}_{0.1}\text{TiSe}_2$ is caused by the spin polarization of states at the Fermi level.

Figure 2 shows the Cr $2p$ core-level photoemission spectra of the $\text{Cr}_{0.1}\text{TiSe}_2$ and $\text{Cr}_{0.33}\text{TiSe}_2$ compounds. In the spectrum of the $\text{Cr}_{0.1}\text{TiSe}_2$ compound, the Cr $2p_{3/2}$ line is split as a result of a strong exchange magnetic interaction between Cr $2p_{3/2}$ holes and spin-polarized Cr d electrons [7]. This is in agreement with the band calculations performed in [11], according to which the exchange splitting of this line is approximately equal to 0.9 eV. On the other hand, no splitting is observed in the spectrum of the $\text{Cr}_{0.33}\text{TiSe}_2$ compound. However, the maximum of this line appears to be flattened; i.e., it retains indications of the splitting observed in the concentration range $x < 0.25$. Such a situation can occur when the broadening of the Cr $3d$ spin subbands is larger than the splitting. In turn, this can be interpreted as resulting from the increase in the overlap of the wave functions of chromium atoms due to the percolation in the sublattice of the Ti–Cr–Ti centers.

Moreover, the width of the Ti $2p$ line in the spectrum of the $\text{Cr}_{0.33}\text{TiSe}_2$ compound is considerably larger than that in the spectrum of the $\text{Cr}_{0.1}\text{TiSe}_2$ compound, whereas the energy positions of these lines coincide with each other (Fig. 3). This can be explained by the fact that the latter compound contains only identical isolated Ti–Cr–Ti centers. As the impurity concentration increases above the percolation threshold, the existence of both isolated and closely spaced centers becomes quite possible.

Therefore, the extension of orbitals of Ti–Cr–Ti centers in Cr_xTiSe_2 compounds can be estimated to be approximately equal to the lattice parameter a_0 .

Upon intercalation, the lattice distortion of Fe_xTiSe_2 compounds is somewhat greater than that of Cr_xTiSe_2 compounds (0.135 and 0.133 Å, respectively) [5]. Conse-

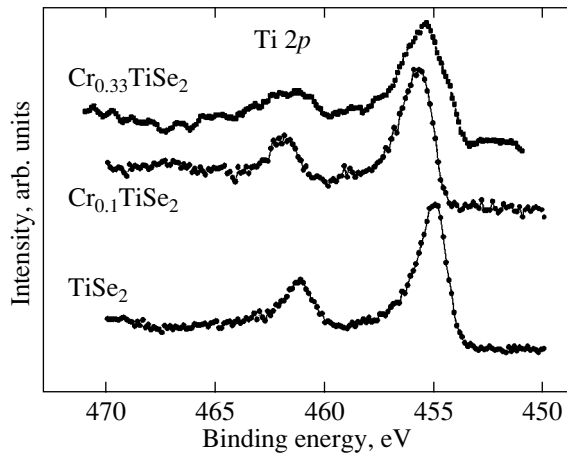


Fig. 3. Ti 2*p* photoemission spectra of the $\text{Cr}_{0.1}\text{TiSe}_2$ and $\text{Cr}_{0.33}\text{TiSe}_2$ compounds. The Ti 2*p* photoemission spectrum of the TiSe_2 initial compound is shown for comparison.

quently, it can be expected that the degree of localization of electrons in Fe_xTiSe_2 compounds should be slightly higher than the degree of their localization in Cr_xTiSe_2 compounds. Actually, an increase in the impurity content $x > 0.25$ manifests itself only in a kink in the dependence $c_0(x)$. At the same time, an increase in the lattice parameter c_0 is observed in the concentration range at $x = 0.5$, which corresponds to the percolation in the intercalant sublattice rather than in the sublattice of Ti–Fe–Ti centers. This can also be explained by the broadening of the impurity band, as is the case in the Cr_xTiSe_2 compounds. However, in the Fe_xTiSe_2 compounds, this broadening can be caused by the direct overlap of orbitals of iron atoms. Since the lattice parameter c_0 begins to increase at an impurity content slightly less than $x = 0.5$, the extension of iron orbitals most likely exceeds the lattice parameter a_0 . It should also be noted that, when the impurity content x approaches 0.5, the concentration of Ti–Fe–Ti centers tends to unity. None of the known types of plane lattices has a percolation threshold corresponding to such a concentration of localization centers. Therefore, the direct overlap of the iron orbitals is the sole possible explanation for the concentration dependence $c_0(x)$ of the Fe_xTiSe_2 compounds. The orbitals of Ti–Fe–Ti centers do not overlap in any of the cases. Hence, the extension of these orbitals is considerably smaller than the lattice parameter a_0 .

It is evident that, in materials with a greater lattice strain, such as Ni_xTiSe_2 compounds, the orbitals of Ti–Me–Ti centers should not overlap. Indeed, the lattice parameter c_0 for these compounds decreases in the intercalant concentration range $0 < x < 0.5$ [9].

The concentration dependence of the lattice parameter $c_0(x)$ for the Co_xTiSe_2 compounds exhibits only an insignificant kink. This suggests that the percolation

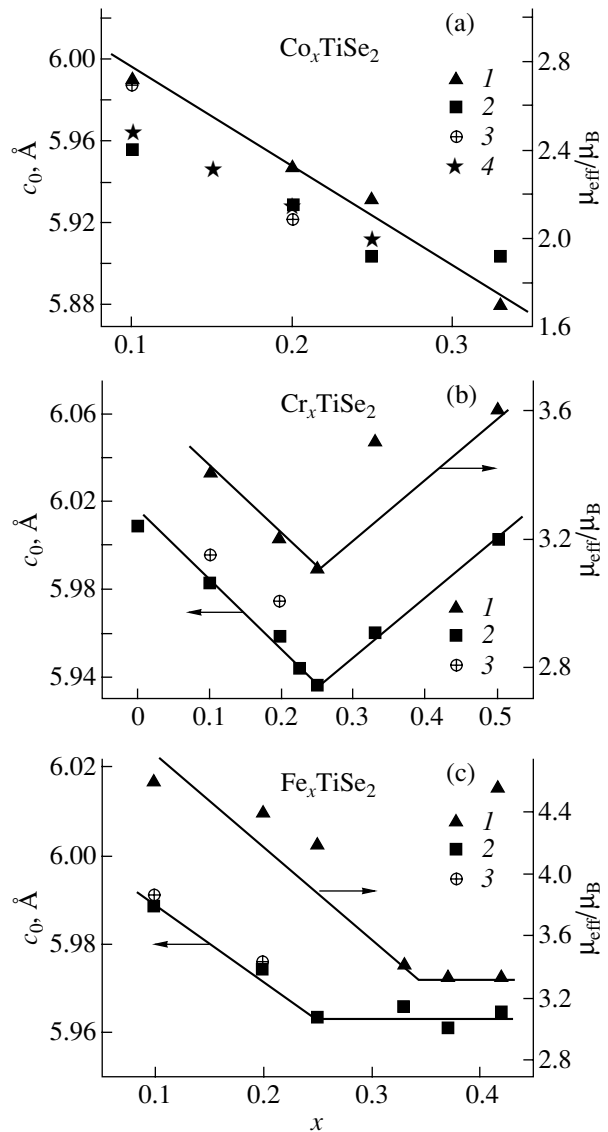


Fig. 4. Concentration dependences of (1) the lattice parameter c_0 and the effective magnetic moment μ_{eff} according to the data obtained in this work and data taken from (2) [2], (3) [12], and (4) [9].

can proceed through the mechanism of overlap of distortion fields around the Ti–Co–Ti covalent centers. No indications of the percolation mechanisms associated with the overlap of orbitals are revealed. Therefore, we can conclude that an intercalated impurity atom affects the electronic structure in the vicinity of the site occupied by the cobalt atom and this effect becomes negligible outside the unit cell.

The kink observed in the concentration dependence of the lattice parameter $c_0(x)$ for the Cr_xTiSe_2 compounds is obviously associated with the overlap of orbitals of titanium atoms coordinated by chromium atoms [mechanism (3)]. However, this mechanism is masked by the percolation due to the overlap of distort-

Effective magnetic moments μ_{eff} (in Bohr magnetons) of impurity atoms intercalated into TiSe_2 and theoretical spin magnetic moments μ_{sp} for charge states of intercalated atoms in the high-spin configuration (S is the spin, q is the spectroscopic splitting factor)

Compound	μ_{eff}	Charge state	$\mu_{\text{sp}} = q\sqrt{S(S+1)}$
Fe_xTiSe_2	5.11	Fe^{2+}	4.90
Co_xTiSe_2	3.18	Co^{2+}	3.87
Cr_xTiSe_2	3.6	Cr^{3+}	3.87

tion fields and, therefore, cannot be identified with certainty.

The Fe_xTiSe_2 system is intermediate between the Co_xTiSe_2 and Cr_xTiSe_2 systems. The kinks in the dependence $c_0(x)$ at contents $x = 0.25$ and 0.5 are caused by the overlap of distortion fields and orbitals of iron atoms, respectively.

The concentration dependences of the effective magnetic moment μ_{eff} and the lattice parameter $c_0(x)$ for the materials under investigation are plotted in Fig. 4. It can be clearly seen from this figure that the concentration dependences of the effective magnetic moment $\mu_{\text{eff}}(x)$ for all compounds are parallel to the concentration dependences of the lattice parameter $c_0(x)$. Consequently, the mechanism responsible for the reduction of the magnetic moments of impurity atoms is governed solely by the broadening of spin subbands due to the hybridization of impurity orbitals with orbitals of the environment according to the Anderson model [8].

On this basis, we can solve the problem regarding the determination of the charge and spin states of intercalated impurity atoms. This problem has long been discussed in the literature. The point is that the experimental dependence of the effective magnetic moment μ_{eff} on the intercalant concentration did not permit one to identify this moment with any standard state of transition metal ions [12] and could be interpreted in different ways. The true effective magnetic moment μ_{eff} can be obtained by extrapolating the concentration dependence of the effective magnetic moment $\mu_{\text{eff}}(x)$ to the impurity content $x = 0$, which corresponds to an infinitesimal concentration of intercalated metal atoms. The effective magnetic moments thus determined are presented in the table. The table also presents the magnetic moments of free ions. It can be seen that the effective

magnetic moments μ_{eff} agree well with the theoretical values for Cr^{3+} , Co^{2+} , and Fe^{2+} charge states of the intercalated impurity atoms in the high-spin configuration.

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REFERENCES

1. A. N. Titov and A. V. Dolgoshein, *Fiz. Tverd. Tela (St. Petersburg)* **40** (7), 1187 (1998) [*Phys. Solid State* **40**, 1081 (1998)].
2. A. Titov, S. Titova, M. Neumann, V. Pleschchev, Yu. Yarmoshenko, L. Krasavin, A. Dolgoshein, and A. Kuranov, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **311**, 161 (1998).
3. A. V. Kuranov, V. G. Pleshchev, 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)].
4. V. G. Pleshchev, A. N. Titov, and A. V. Kuranov, *Fiz. Tverd. Tela (St. Petersburg)* **39** (10), 1618 (1997) [*Phys. Solid State* **39**, 1442 (1997)].
5. A. N. 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. M. F. Sykes and J. W. Essam, *Phys. Rev. Lett.* **10**, 3 (1963); *J. Math. Phys.* **5**, 1117 (1964).
7. A. N. Titov, A. V. Kuranov, V. G. Pleshchev, Yu. M. Yarmoshenko, M. V. Yablonskikh, A. V. Postnikov, S. Plogmann, M. Neumann, A. V. Ezhov, and E. Z. Kurmaev, *Phys. Rev. B* **63**, 035106 (2001).
8. P. W. Anderson, *Phys. Rev.* **124** (1), 41 (1961).
9. Y. Arnaud, M. Chevreton, A. Ahouanjiou, M. Danot, and J. Rouxel, *J. Solid State Chem.* **18**, 9 (1976).
10. V. G. Pleschov, N. V. Baranov, A. N. Titov, K. Inoue, M. I. Bartashevich, and T. Goto, *J. Alloys Compd.* **320**, 13 (2001).
11. A. V. Postnikov, M. Neumann, St. Plogmann, Yu. M. Yarmoshenko, A. N. Titov, and A. V. Kuranov, *Comput. Mater. Sci.* **17** (2–4), 450 (2000).
12. Y. Tazuke and T. Takeyama, *J. Phys. Soc. Jpn.* **66**, 827 (1977).

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