

## Influence of structural disorder on the magnetic, optical, and transport properties of $\beta$ -phase $\text{Co}_{0.50}\text{Ti}_{0.50}$ alloy films

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The influence of the structural disorder on the magnetic, optical, and transport properties of the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films has been investigated. The disordered state in the alloy films was obtained by vapor-quenching deposition onto substrates cooled by liquid nitrogen. The transport properties of the ordered and disordered alloy films have been measured in a temperature range of 4.2–300 K. The optical properties were measured by spectroscopic ellipsometry at 293 K in an energy range of 0.5–4.7 eV. The experimental optical data of the ordered CoTi compound were compared with the results of *ab initio* calculations made by using the linearized-augmented plane-wave method with the local-density approximation, and explained in terms of the electronic energy band structure. An excellent agreement between the experimental and calculated optical conductivity spectra of the ordered compound was achieved by the inclusion of the quasiparticle self-energy correction. It was shown that the disordered state in the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy film is ferromagnetically ordered at 100 K. The changes in the electronic structure of the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy caused by the order-disorder structural transformation are explained on the analyses of the measured optical and resistivity data. [S0163-1829(99)00735-3]

### I. INTRODUCTION

The electronic structures, physical properties, and thermal stability of  $3d$  transition-metal compounds in connection with peculiarities of their crystalline structures have been a focus of many investigations during recent years.

$\beta$ -phase Co-Ti alloys have a CsCl-type ( $B2$ ) crystal structure that exists at 873 K in a Ti concentration range of 49.5–54.2 at. % and that is stable up to the melting point (1508 K).<sup>1</sup> In the perfectly ordered equiatomic CoTi alloy the Co and Ti atoms form interpenetrating primitive cubic lattices where each Co atom has eight Ti atoms as the nearest neighbor and vice versa. Because of the significant charge transfer from Ti to Co, in other words, the significant ionic contribution to the metallic bonding this alloy is very stable in a wide-temperature range. The nature of the high stability of CoTi compound has been discussed in Ref. 2 in terms of band filling. The magnetic measurements and the spin-polarized linear-muffin-tin-orbital (LMTO) calculation of the ordered CoTi alloy have shown that this compound is paramagnetic with no magnetic moment of the Co atoms.<sup>3,4</sup> It is also supposed that such a magnetic behavior of CoTi compound is arisen from the specific local environment.<sup>3</sup>

In contrast to the ordered state of CoTi alloy, the Co and Ti atoms can randomly occupy the sites of bcc lattice in the disordered state. It should be expected that this change in symmetry and basis of the unit cell itself will lead to drastic changes in electronic energy structures (EES) and physical properties of this alloy.

It is well known that optical spectroscopy is a rather sensitive tool for studying the EES in the region of a few eV

near the Fermi level and that the optical properties of metals depend strongly on their EES, which are correlated with the atomic and magnetic ordering.

There are only a few publications devoted to the experimental study of the optical properties of the bulk-ordered equiatomic CoTi alloy.<sup>5–7</sup> All the measured optical conductivity (OC) spectra showed a close resemblance to each other above 1.5 eV, but some problems with the experimental study of the optical properties of CoTi compound still exist in the low energy region. The measured OC spectrum for the ordered CoTi alloy<sup>6</sup> does not reveal an absorption peak in the near infrared (IR) region as predicted by the theoretical calculation.<sup>7</sup> According to Sasovskaya<sup>6</sup> the low-energy quantum absorptions were observed for  $\text{Ti}(\text{Fe}_x\text{Co}_{1-x})$  pseudobinary alloys ( $x=0.3, 0.5, \text{ and } 0.8$ ) in an energy range of 0.2–0.6 eV, but absent for CoTi compound. Sasovskaya attributed the emergence of this peak in these pseudobinary alloys to the interband transitions between virtual bound states, which result from the antistructure Fe atoms (Fe-ASA), the Fe-atoms at the Ti sites. Thus, additional experimental study of the optical properties even for the ordered CoTi compound mainly in the near IR region seems to be desirable.

An unambiguous interpretation of the experimental optical spectra requires *ab initio* calculations of the electronic structures of the substance. The aim of the theoretical analysis is to assign the experimentally observed spectral features to specific electronic excitations in the Brillouin zone (BZ).

The electronic structure and some physical properties of  $B2$ -phase CoTi have been calculated several times.<sup>2,4,7–10</sup> Among all these publications the calculated optical proper-

ties were presented only in Refs. 7 and 10. In contrast to Yegorushkin and Fedyanova,<sup>10</sup> Rhee *et al.*<sup>7</sup> included the dipole-transition-matrix elements, which are very important for the accurate calculation of the OC spectrum. In Ref. 7 it was also shown that the agreement between the measured and calculated spectra was markedly improved by the inclusion of the quasiparticle self-energy corrections. The knowledge of the nature of the absorption peaks in the OC spectra of the ordered compounds opens the perspectives for the experimental study of the peculiarities in the EES of the disordered alloys by tracing the gradual reconstruction of the absorption peaks caused by the structural disordering. To the best of our knowledge the optical properties of the disordered equiatomic CoTi alloy have not been investigated yet.

The theoretical calculations of the density of states (DOS) and the magnetic moment for the disordered  $\text{Co}(\text{Ti}_{1-x}\text{Al}_x)$  alloys with  $0 < x < 1$  was performed by the tight-binding LMTO method within the coherent-potential approximation.<sup>4</sup> It was shown that for the equiatomic CoTi alloy in the disordered state the magnetic moment of the Co atoms is equal to zero. This theoretical prediction agrees with the results of an experimental study by Endo *et al.*<sup>5</sup> On the other hand, we suspect whether the significantly disordered state in bulk CoTi alloy was obtained or not because of the high thermal stability of this compound.

It is well known that thin-film technology allows us to prepare metals and alloys in various metastable states, which sometimes cannot be obtained in bulk materials. Therefore, it seems to us very attractive to apply thin-film technology in obtaining CoTi alloy in the disordered state for the purpose of studying the various physical properties of the disordered CoTi alloy. It can be expected that the significant structural disorder and the arbitrary occupation of the sites of bcc lattice by the Co and Ti atoms change the local environment and create a chance of appearance of single Co-ASA or their clusters in CoTi alloy and, hence, cause some changes in the magnetic state of alloy.

Taking into account a steep energy dependence of the DOS of CoTi compound near the Fermi level, it is also expected that an influence of the structural disorder in Co-Ti alloy on the transport properties is significant. We have already investigated various physical properties of the B2-phase Co-Al alloys<sup>11–13</sup> and Fe-Al alloys<sup>14–16</sup> and observed some significant changes in physical properties upon the order-disorder structural transformation. We attributed those changes to the formation of transition metal ASA, resulting in a formation of magnetic clusters, and to the substantial increase of localized states near the Fermi level. To the best of our knowledge, the effect of the structural disorder on the resistivity of CoTi alloy has not been investigated yet, either.

Thus, the purpose of this paper is to obtain the equiatomic CoTi alloy in the disordered state and to study experimentally the influence of the structural order-disorder transformation on various physical properties, aiming the analysis of changes in the EES of alloy resulted from such a structural transformation.

## II. EXPERIMENTAL PROCEDURE

$\beta$ -phase  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy was prepared by melting Co and Ti pieces of 99.99% purity in an arc furnace with a

water-cooled Cu hearth. In order to obtain the volume homogeneity the ingot was remelted twice and then annealed at 1300 K for 6 h. Any weight loss after the repeated melting and heat treatment was not observed.

As aforementioned, the ordered state of CoTi alloy is very stable, and all our preliminary attempts to obtain bulk alloy in the disordered state by quenching from high temperatures had no success. Therefore, in order to prepare the disordered alloy, the advantages of thin film technology were employed.

$\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films with a total thickness of about 100 nm and of  $10 \times 30$  mm in dimensions were prepared by flash evaporation of the crushed alloy powders of 80–100  $\mu\text{m}$  in diameter simultaneously onto glass, and single-crystalline Si and NaCl substrates in high vacuum conditions better than  $5 \times 10^{-5}$  Pa. The thin film samples deposited onto glass and Si substrates were mainly used for the measurements of the optical, transport, and magnetic properties, while the films deposited onto NaCl substrates were used for the structural study.

The deposition rate was about 2 nm/s. Such a high deposition rate was chosen to reduce the volume contamination and oxidation of the films. An equilibrium ordered  $\beta$  phase in these films was reached by the deposition onto heated substrates up to 730 K (state 1).

In order to obtain a disordered state in the film, a vapor-quenching-deposition technique was employed, where a chaos of gas phase is condensed onto substrates cooled down to 150 K by liquid nitrogen (state 2). All the films prepared at 150 K were cut into two parts and one set of halves was put into a vacuum chamber and annealed at 730 K for 45 min in a high vacuum of  $1 \times 10^{-5}$  Pa (state 3).

X-ray fluorescence of the prepared samples confirmed their equiatomic composition. Structural analysis of the films was performed by using transmission electron microscopy (TEM).

The optical constants (the real and imaginary parts of the complex refractive index,  $\tilde{N} = n - ik$ ) of the samples were measured by the polarimetric Beattie technique<sup>17</sup> at room temperature (RT) in a spectral range of 265–2500 nm (4.7–0.5 eV) at a fixed incidence angle of 73°. The obtained values of  $n$  and  $k$  were used for calculation of the real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the diagonal components of the complex dielectric tensor ( $\tilde{\epsilon}_{xx} = \tilde{\epsilon}_{yy} = \tilde{\epsilon}_{zz} = \epsilon_1 - i\epsilon_2$ ), and OC ( $\sigma$ ) using the appropriate expressions;  $\epsilon_1 = n^2 - k^2$ ,  $\epsilon_2 = 2nk$  and  $\sigma(\hbar\omega) = \epsilon_2\omega/4\pi$  where  $\omega$  is the angular frequency of the incident photon.

The resistivity measurements were carried out by using the four-probe technique in a temperature range of 4.2–300 K. Magnetic properties of the ordered and disordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  films were investigated by using a vibrating sample magnetometer (VSM) at 100 K and room temperature (RT) in the parallel (to the film surface) configuration.

## III. RESULTS AND DISCUSSION

TEM pattern for the film deposited onto the substrate at 730 K exhibits a mixture of diffraction rings typical for bcc lattice and a series of additional superstructure rings, which are attributed to the reflections from the (100), (111), and (210) atomic planes. The mean grain size is about 50 nm. This result shows that a stable phase of the superlattice with

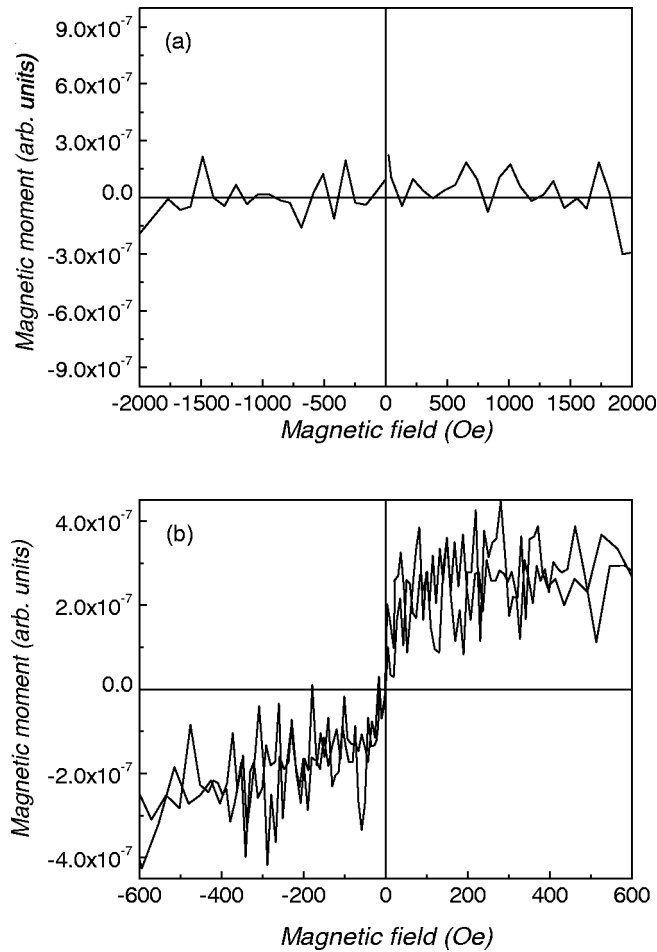


FIG. 1. Experimental magnetization loops for the disordered  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films at (a) 300 K and (b) 100 K, respectively.

a high degree of long-range order ( $\eta$ ) is formed at our deposition conditions, even though  $\eta_1$  of the state (state 1) can not be estimated quantitatively.

A decrease in substrate temperature to 150 K leads to the formation of a considerably disordered polycrystalline alloy films without any visible superstructure rings (state 2,  $\eta_2 \sim 0$ ) and the mean grain size is less than 5 nm. An annealing of these disordered films at 730 K for 45 min caused a recovery of the structural rings and an appearance of weak (tiny) superstructural diffraction rings typical for the B2 structure. However, comparing with the ordered films, the intensity ratio of the superstructural diffraction rings to the structural ones is lower. Therefore, it is clear that  $\eta_3$  in such a film (state 3) is smaller than  $\eta_1$ . Thus, it can be concluded that such a deposition technique and additional heat treatment allow us to prepare a set of  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films with various degrees of long-range order:  $\eta_1 \sim 1 > \eta_3 > \eta_2 \sim 0$ .

According to the results of the magnetization study using VSM, the ordered  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films are not ferromagnetically ordered at least above 100 K. The disordered state in the  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films is neither ferromagnetically ordered at 300 K, but a decrease in measurement temperature down to 100 K leads to the appearance of a small magnetic moment (see Fig. 1). Unfortunately, owing to a difficulty in the precise measurement of the film thickness we could not determine the magnetic moment quantitatively. Such a mag-

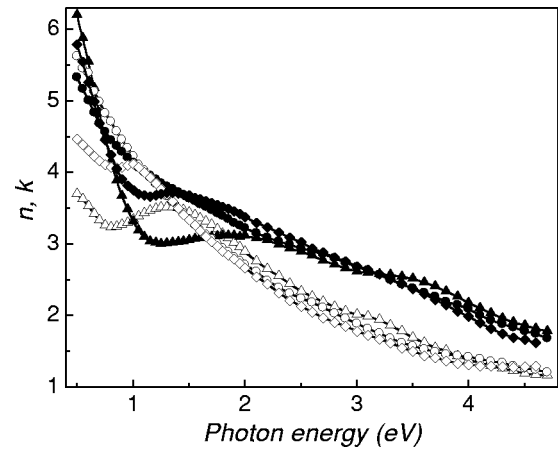


FIG. 2. Experimental spectra of the real ( $n$ : open symbols) and imaginary ( $k$ : solid symbols) parts of the complex refractive index for  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films deposited at 150 K (circles), deposited at 150 K and annealed at 730 K for 45 min (diamonds), and deposited at 730 K (triangles).

netic behavior of the  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films allows us to draw a deduction that the local environment plays a very important role in determining the magnetic properties.

The experimental  $n$  and  $k$ ,  $\sigma$ , and  $\epsilon_1$  spectra of the  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films with different  $\eta$  are shown in Figs. 2, 3, and 4, respectively.

The optical constants  $n$  and  $k$  of the ordered  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films increase continuously with decreasing photon energy, except a region of anomalous dispersion, which is located between 0.7–2 eV. Such a behavior of  $n$  and  $k$  reflects the existence of an interband absorption in this spectral region. The decrease in long-range order of the  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films leads to a decrease of the spectral interval relevant to the anomalous dispersion of the optical constants. For the completely disordered  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films this region is not observed.

The  $\sigma$  curves for all the investigated  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films have a strong absorption peak in the visible region of spectra, labeled by B, and two shoulders on the low- and

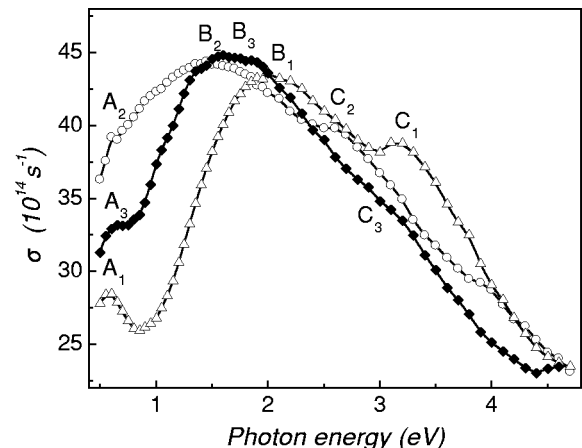


FIG. 3. Experimental optical conductivity spectra for  $\text{Co}_{0.5}\text{Ti}_{0.5}$  alloy films deposited at 150 K (circles), deposited at 150 K and annealed at 730 K for 45 min (diamonds), and deposited at 730 K (triangles).

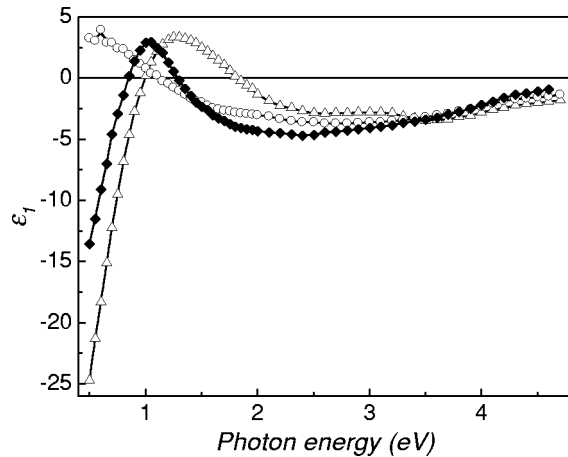


FIG. 4. Experimental  $\epsilon_1$  spectra for  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films deposited at 150 K (circles), deposited at 150 K and annealed at 730 K for 45 min (diamonds), and deposited at 730 K (triangles).

high-energy sides of the main peak; features A and C, respectively. For the ordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films the peaks  $A_1$ ,  $B_1$ , and  $C_1$  are clearly exhibited and their maxima are located at 0.6, 2.0, and 3.1 eV, respectively. In contrast to the OC spectrum, the experimental  $\epsilon_1$  spectrum of the ordered film reveals no prominent features, intersecting the zero line twice at 0.98 and 1.82 eV and reaching its maximum at 1.30 eV. Below 0.98 eV  $\epsilon_1$  is negative and increases in absolute value with decreasing photon energy. This indicates a significant contribution to the optical absorption from free carriers.

The overall shape of the measured OC spectrum of the ordered sample is in a good agreement with the experimental data for the bulk ordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy,<sup>5,7</sup> as well as with a calculated OC spectrum.<sup>7</sup> Both experimental OC spectra of the bulk samples showed clearly manifested absorption peaks at 2.15 and 3.05 eV in Ref. 5 and also at 2.15 and 3.15 eV in Ref. 7.

The calculated optical conductivity spectrum with broadening of CoTi compound produces the similar shape to the experiment with the peak positions at higher energies than the measured ones (compare the calculated curve without self-energy correction with the experimental curves in Fig. 5). This is quite usual for transition metals<sup>18</sup> and their intermetallic compounds. It is believed to be due to changes in the energy of excited states near the Fermi level relative to the energy calculated from the ground-state potential.<sup>18</sup> This effect motivated the consideration of an approximate self-energy correction explained in detail elsewhere.<sup>19</sup> By applying this single-parameter self-energy correction, we were able to produce the spectrum with the peaks located at the same energies as the measured ones. The corrected theoretical OC spectrum exhibits absorption peaks marked by  $A_t$ ,  $B_t$ , and  $C_t$  and located at 0.58, 2.15, and 3.30 eV, respectively (see Fig. 5). It should be noted that the locations of the high-energy absorption peaks for the ordered CoTi alloy films in Fig. 3 are slightly shifted to the low-energy side in comparison with the bulk-ordered samples. A possible reason for this shift is discussed below.

The calculated band structure along the high-symmetry lines for the ordered CoTi alloy is shown in Fig. 6. The detailed analysis of the band structure for the ordered CoTi

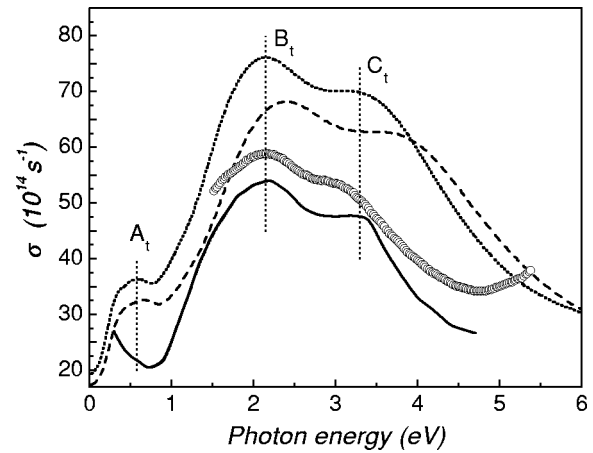


FIG. 5. The calculated (broadened) OC spectra of the B2-phase CoTi, with (short-dash) and without (dash) self-energy correction together with the experimental OC spectra for the bulk ordered samples from Refs. 5 (solid) and 7 (circles). Note that the zero of OC is suppressed.

compound can be found elsewhere.<sup>7</sup> The low-energy peak A undergoes the most significant changes upon the order-disorder transformation as seen in Fig. 3. This peak arises from the electronic excitations from the sixth to the seventh band or from the seventh to the eighth band in the vicinity of point  $M$  and in the  $X$ - $M$ - $R$  plane (see Fig. 6). The occupied bands have mainly the Co  $d$  character with a significant admixture of the Ti  $d$  character and the unoccupied bands have a mixture of the  $p$  and  $d$  characters of both atoms. Very strong transitions from the seventh band to the ninth band also exist along the  $X$ - $R$  line. The occupied band has dominantly the Co  $d$  character with a small admixture of the Ti  $d$  character, while the unoccupied band has mainly the Co  $d$  character with a significant admixture of the Ti  $d$  character. Although the dipole-transition-matrix element could be quite small because of the band characters, the two bands are quite parallel, resulting in a large joint density of states and, hence, considerable contributions to the OC.

These bands responsible for peak A are placed near the Fermi level, therefore, even an insignificant raising of the

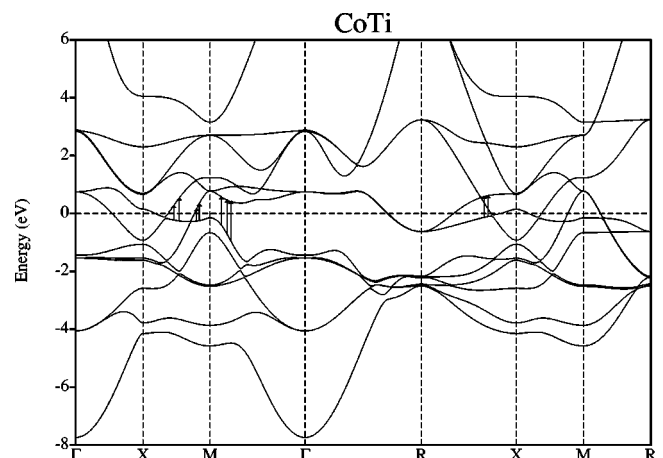


FIG. 6. Energy bands for CoTi. The Fermi level is located at zero energy. The electron transitions responsible for absorption peak A are shown by arrows.



occupied band or lowering of the unoccupied band induced by the order-disorder transformation leads to a disappearance of the occupied or empty states in this energy range, and hence, to the vanishing of this absorption peak as in Fig. 3.

According to Ref. 7 absorption peak  $B_t$  in the calculated OC spectrum is related to the electron transitions from bands 4, 5, and 6 to bands 9 and 10 on the  $\Gamma$ - $X$ - $M$  line. The contributions from  $\mathbf{k}$  points of the same bands on the  $R$ - $X$  line to the formation of the  $B$  absorption peak are also significant because these bands are almost parallel. The high-energy absorption peak  $C$  is mainly due to the electronic transitions between bands 4 and 5, and band 11 at  $\mathbf{k}$  points on the  $\Gamma$ - $X$ - $M$  line and in the neighborhood. The initial states of these excitations have mainly the Co  $d$  character with an admixture of the Ti  $d$  character.<sup>7</sup>

A loss of the translational invariance caused by the order-disorder structural transformation results in significant changes in the optical properties of the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films. Absorption peaks  $B$  and  $C$  move to lower energies by about 0.55 and 0.50 eV, respectively; peak  $A$  does not change its location but is nearly vanished as seen in Fig. 3. The intensities of the peaks (except  $A$ ) are not changed significantly.

Remarkable changes in  $\varepsilon_1$  spectrum are also observed at  $\hbar\omega < 2.0$  eV (see Fig. 4); the real part of the dielectric function changes its sign at 1.13 eV from negative to positive one in case of the disordered film. It is commonly known that, in metals, the negative value of  $\varepsilon_1$  in near IR region is caused by the acceleration mechanism of free electrons, while the positive contribution to  $\varepsilon_1$  is usually concerned with the interband transition of bound electrons.<sup>20</sup> Thus, the observed behavior of the  $\varepsilon_1$  spectrum for the disordered state of alloy allows us to conclude that the structural disorder makes the electrons more localized than in the ordered state.

The influence of the atomic ordering in the diatomic linear chains on the EES was investigated by Krivoglaz and Smirnov.<sup>21</sup> A similarity of the formation of a forbidden gap caused by the atomic ordering could be presumed for the EES of one- and three-dimensional lattices. In case of the order-disorder transformation in a CsCl lattice the period of translation is changed only along the diagonals of the cube, that is, in the (111) direction in the real space. Therefore, we can expect that the BZ of the ordered  $B2$ -type structure has new gaps (in comparison with the disordered state) due to the appearance of new BZ boundaries (BZB) which pass through the  $X$  point of the reciprocal space.

A large portion of the electronic transitions responsible for the aforementioned peaks ( $A$ ,  $B$ , and  $C$ ) are due to the electronic excitations occurred in the vicinity of the  $X$  point. The transition from the CsCl to the bcc symmetry (the order-disorder structural transition) leads to a modification of the translational periodicity in the (111) direction in the real space and, hence, to the vanishing of the BZB, which pass through the  $X$  point in the BZ for simple cubic. This causes some energy gaps at the  $X$  point to disappear, for example,  $X'_4$ - $X_1$  between the first and the second bands,  $X_2$ - $X_5$  between the third and the fourth bands, and so on.

If the deformations of both the occupied and empty bands taking part in the formation of an interband absorption peak, caused by the gap vanishing, are the same, the position of the absorption peak is preserved in the OC spectrum, but this is

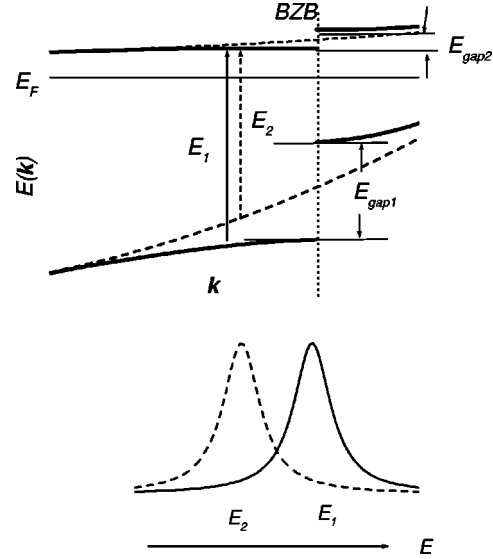


FIG. 7. Schematic drawing of the band structure near the BZB for the ordered (thick solid line) and disordered (dashed line) states. The Fermi level is shown by thin solid line. The interband electron transitions for the ordered and disordered states are shown by solid and dashed arrows, respectively. The lower part of the figure presents schematically the locations of the absorption peaks for the ordered ( $E_1$ ) and disordered ( $E_2$ ) states.

usually not the case. Therefore, the disappearance of the energy gaps near the  $X$  point in the disordered state of alloy leads to different deformations of the involved bands and causes mainly a reduction of the energy difference between the states involved in the formation of the  $B$  and  $C$  absorption peaks. These changes in  $E(\mathbf{k})$  result in shifts of the peaks to the lower energy side as in Fig. 3. This process is shown schematically in Fig. 7.

The observed changes in the optical properties of the CoTi alloy caused by the structural disorder can also be discussed partly in terms of the DOS. The calculated DOS curve for CoTi compound exhibits two main peaks; the Co  $t_{2g}$  band with a small admixture of the Ti  $e_g$  band, which extends from 4 to 1 eV below the Fermi level, and the slightly Ti  $e_g$  band located from 1 eV below to 4 eV above the Fermi level. This manifold is also admixed with the Co  $t_{2g}$  character. The mentioned manifolds are separated by a deep minimum or “pseudogap” caused by the fact that the nearest neighbors of Co in the ordered alloy are the Ti atoms.

The band-by-band decomposition of peaks  $A_t$ ,  $B_t$ , and  $C_t$  of the calculated OC spectrum allows us to determine the initial- and final-energy intervals responsible for these peaks and we can correspond the experimentally observed absorption peaks with electron excitations between the occupied and empty bands. These transitions are indicated in Ref. 7. Peaks  $B_t$  and  $C_t$  turned to be formed mostly by the interband transitions between  $t_{2g}$  and  $e_g$  manifolds, while absorption peak  $A_t$  arises from the electronic transitions within the  $e_g$  manifold.

In case of the arbitrary occupation of the sites of bcc lattice (in the disordered state), the Co ions become the nearest neighbors with a higher probability than in the ordered state. As a result the  $e_g$ - $t_{2g}$  splitting becomes smaller and

these manifolds become closer. This leads to the shift of the interband absorption peaks *B* and *C* to the low-energy side.

The suggested explanation in terms of the DOS are further supported by the results of the theoretical calculations of the DOS for the ordered<sup>7</sup> and disordered<sup>4</sup> CoTi alloy; the energy interval between main peaks in the DOS curve for the disordered state of alloy is smaller than that for the ordered one. This confirms that the structural disorder in the CoTi equiatomic alloy reduces the splitting between  $e_g$  and  $t_{2g}$  manifolds.

However, peak *A* evolves differently because the bands participating in the transitions responsible for this peak have different characteristics from those of peaks *B* and *C*. The initial (occupied) and/or final (unoccupied) bands are closely located to the Fermi level (see Fig. 6) and are not severely affected by the structural order-disorder transition. Therefore, peak *A* is not likely to change its energy position upon transition. Instead, it may disappear because of the shift of the Fermi level itself, which may make the initial (final) state unoccupied (occupied), prohibiting the optical transitions.

The shift of the interband absorption peaks can be also caused by a changes in the mean interatomic distance due to the structural disordering. The first-principle calculations of the optical properties of CoTi compound show that a shift of the *B* and *C* peaks by 0.25 eV to the low-energy side with respect to the ordered state can be made by increasing the lattice parameter by 3%. This value seems to us too much for such kind of structural transformation, and therefore, the increase in the mean interatomic distance (if any) in the disordered state of alloy is not enough to explain all the observed changes in the optical properties.

Likewise, we explained qualitatively the experimentally observed variations of the optical properties in terms of the influence of disordering on the width of the ‘‘pseudogap’’ and the alteration of the Fermi level, and partially the increase in mean interatomic distance.

The formation of the disordered state in the CoTi alloy film by using the vapor-quenching deposition is accompanied by a decrease in the mean grain size. The grain boundaries are usually highly disordered or even amorphous. It was established above that the structural disorder leads to the shifts of the absorption peaks to the low-energy side. Even perfectly ordered film has much smaller grain size than the bulk material. Therefore, the aforementioned shift of the high-energy absorption peaks of the ordered alloy film with respect to the bulk sample could be explained by finer grain structures in the film sample than the bulk one.

An annealing of the disordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films at 730 K for 45 min induced a partial ordering. The intermediate degree of long-range order makes us understand the behavior of their optical properties. It is seen that all the spectral dependencies of the optical properties of the annealed sample are in between the corresponding curves for the ordered and disordered alloy films (see Figs. 2–4).

Evidently, two possible mechanisms of the ordering in such a metastable disordered film caused by the annealing can be assumed; (i) an emergence of nuclei for the perfectly ordered phase in the disordered matrix and a growth of the volume of these nuclei, or (ii) a gradual increase in the degree of the long-range order in the whole volume of the film. To our mind, the first one is more probable. To confirm this

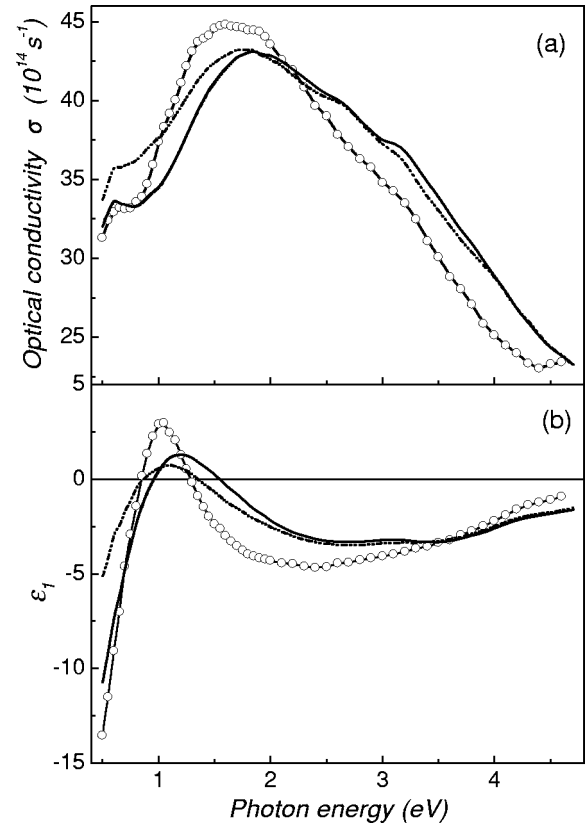


FIG. 8. Simulated (a) OC and (b)  $\epsilon_1$  spectra of two-phase system with 30% (dash-dot-dot) and 50% (solid) of the ordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  phase in the disordered matrix. Circles present the corresponding experimental spectra of  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films deposited at 150 K and annealed at 730 K for 45 min.

presumption, a simulation of the optical properties of two-phase system (a mixture of completely ordered particles of alloy in the disordered matrix with various contents of the particles) has been carried out in the framework of the effective medium approximation. The results are presented in Fig. 8. It is seen that there is a reasonable agreement between the simulated and experimental data. A reason why we prefer the first presumption is that peak *A* does not change its location in the simulated OC spectra. Indeed, if this process comes along the other way, the peak location should be changed, following a gradual growth of the corresponding gap with increasing  $\eta$ , but it turns out to be not the case. Therefore, it can be concluded that the process of ordering in such a metastable disordered alloy caused by annealing the films comes with an appearance of the ordered nuclei and their growth.

Figure 9 presents the temperature dependences of the normalized resistivity with respect to that at RT of the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films with various degrees of long-range order, revealing significantly different behavior according to  $\eta$ . The ordered film exhibits a typical metallic behavior with a positive value of the temperature coefficient of the resistivity (TCR). The structural disorder in the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films leads to the change in sign of the TCR from positive to the negative one. It should be also emphasized here that the resistivity of the disordered alloy film is significantly higher than the ordered one in the measured temperature range. The temperature dependence of the resistivity for the  $\text{Co}_{0.50}\text{Ti}_{0.50}$

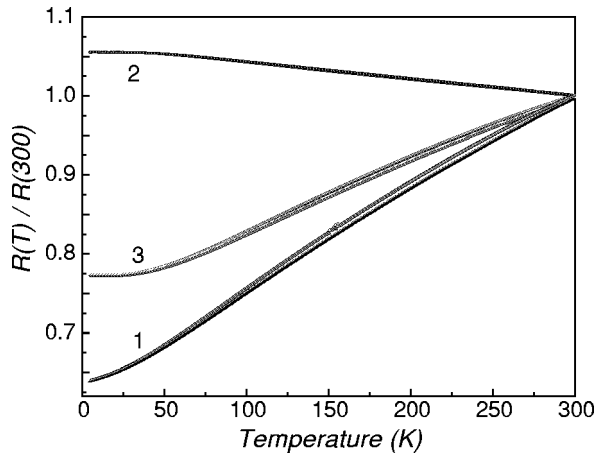


FIG. 9. Variation of the normalized resistivity with temperature for the ordered (1), intermediately disordered (3), and disordered (2)  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films.

alloy film with intermediate  $\eta$  comes in between the ordered and disordered ones.

The peculiarities of the electronic structures of the high resistivity systems responsible for the negative TCR are widely investigated during recent years. It was suggested that the negative TCR concerns with the pseudogap in the EES,<sup>22</sup> Anderson localization of carriers due to the structural disorder,<sup>23,24</sup> and a formation of the virtual band, which is weakly hybridized with the electronic states of matrix.<sup>25</sup> A very similar temperature dependence of the resistivity was observed for annealed and quenched Ti-based V-Ti alloys.<sup>26</sup> While the annealed V-Ti alloys have a positive TCR, the quenched alloys are changed to have the negative one. For the origin of the negative TCR of the quenched V-Ti alloy the authors suggested a formation of the crystalline  $\omega$  phase with some gap in the EES near the Fermi level. The same reason for the appearance of the negative TCR was also noted for the quasicrystal  $\text{Al}_{0.625}\text{Cu}_{0.25}\text{Fe}_{0.125}$ .<sup>27</sup> In Ref. 27, a conclusion was drawn that this alloy is narrow- or zero-gap semiconductor.

It should be mentioned that the negative TCR of the disordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy film is also accompanied by a positive value of  $\epsilon_1$  as in Fig. 4, which reflects a significant variation of the plasma frequency or, equivalently, the effective mass. The plasma frequency  $\omega_p$  is given by

$$\omega_p^2 = \frac{4\pi N e^2}{m^*},$$

where  $N$  is the charge-carrier concentration and  $m^*$  is the effective mass of the charge carrier. The location of zero crossing in the IR region of the  $\epsilon_1$  spectra moves toward the lower energy as the long-range order decreases, and for the disordered sample, the value of  $\epsilon_1$  becomes positive when the photon energy is less than 1 eV. The decrease of the location of the zero crossing is a typical signature for the reduction of the plasma frequency. Since  $N$  does not change appreciably upon the order-disorder transformation, the dominant factor determining  $\omega_p$  is  $m^*$ . The reduction of  $\omega_p$

results from an enhancement of  $m^*$ , and this is, again, due to the dispersionless band which is ascribed to the increased disorderliness. Thus, we can conclude that the evolution of  $\epsilon_1$  spectra and the change of TCR upon the structural transformation are consistently correlated through the increased disorderliness.

This is also supported by the DOS calculated by using the linear-muffin-tin-orbital method for equiatomic CoTi and  $\text{Co}_5\text{Ti}_3$  alloys. For  $\text{Co}_5\text{Ti}_3$  alloy the electronic structures were calculated using a defect-specified supercell method.<sup>28</sup> As the Ti concentration decreases, a very sharp peak in the DOS curve near the Fermi level grows, indicating an easier localization of the states near the Fermi level and an increase of  $m^*$ . This is another manifestation of the localization of the states near the Fermi level upon the order-disorder transformation.

#### IV. SUMMARY

1. The disordered state in the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films was obtained by means of vapor-quenching deposition onto glass substrates cooled by liquid nitrogen. In contrast to the results of previous study,<sup>3</sup> it was shown that the disordered state is ferromagnetically ordered at 100 K.

2. The optical properties of the ordered  $\text{Co}_{0.50}\text{Ti}_{0.50}$  films have been studied experimentally at RT in a photon energy range of 0.5–4.7 eV and compared with the results of the first-principles calculations. The origin of the main absorption peaks has been determined. It was experimentally shown that a low-energy interband absorption peak near 0.6 eV exists in the OC spectrum for the ordered alloy. This result confirms the theoretical calculations for this region of spectra.

3. The loss of the translational invariance in the disordered state leads to significant changes in the magnetic, optical, and transport properties of the  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films.

4. The observed changes in the optical properties caused by the order-disorder structural transition were discussed in the framework of lattice symmetry and electronic structure of the ordered CoTi compound.

5. The observed temperature and structural dependencies of the resistivity of the investigated  $\text{Co}_{0.50}\text{Ti}_{0.50}$  alloy films as well as their optical properties were explained by the partial localization of the electronic states near the Fermi level.

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