

---



---

**CONDENSED-MATTER  
SPECTROSCOPY**

---



---

# Role of Fe and Co in Optical Conductivity and Electronic Structure of TbNi<sub>4</sub>Fe and TbNi<sub>4</sub>Co<sup>1</sup>

Yu. V. Knyazev<sup>a\*</sup>, A. V. Lukoyanov<sup>a, b</sup>, Yu. I. Kuz'min<sup>a</sup>, A. Haldar<sup>c, d</sup>, and K. G. Suresh<sup>c</sup>

<sup>a</sup> Institute of Metal Physics, Russian Academy of Sciences, Ural Branch, Yekaterinburg, 620990 Russia

<sup>b</sup> Ural Federal University, Yekaterinburg, 620002 Russia

<sup>c</sup> Magnetic Materials Laboratory, Department of Physics, IIT Bombay, Mumbai, 400076 India

<sup>d</sup> Presently at S. N. Bose National Centre for Basic Sciences, Kolkata, 700098 India

\*e-mail: knyazev@imp.uran.ru

Received January 16, 2014

**Abstract**—Optical properties of two intermetallic compounds TbNi<sub>4</sub>Fe and TbNi<sub>4</sub>Co have been studied employing ellipsometry in a spectral range 0.22–15 μm to reveal their characteristic features in comparison with the parent compound TbNi<sub>5</sub>. The electronic structure of TbNi<sub>4</sub>Fe and TbNi<sub>4</sub>Co was calculated within the LSDA + *U* method (local spin density approximation with Hubbard *U*-correction). Based on the calculated electronic structure results, the theoretical optical conductivity was calculated and used to interpret experimental conductivity in the range of interband optical absorption.

**DOI:** 10.1134/S0030400X14090124

## INTRODUCTION

The RNi<sub>5</sub> group of compounds where R is a rare earth has been extensively studied due to their interesting magnetic and electrical properties, application in hydrogen storage technology and as adiabatic nuclear cooling agents [1–4]. Compounds of this series with different R have been investigated with various theoretical and experimental techniques. It was found that many physical properties of RNi<sub>5</sub> intermetallics change substantially after replacing Ni with other *d*- or *p*-elements as a result of the significant effect of the substituent on the electronic structure, crystal field and exchange interaction. For example, various pseudobinary RNi<sub>5-x</sub>M<sub>x</sub> alloys with M = *p*- or *d*-metals, which are solid solutions with the structure of the parent binary compound, exhibit substantial concentration dependences of the crystalline, electronic, magnetic and thermodynamic properties [5–7]. It is also well known that substitutions for Ni in binary intermetallic compounds by various metals can drastically influence the hydrogen sorption characteristics.

Substantial modifications of the above properties imparted by an increase of substituent concentration were found also in ferromagnetic TbNi<sub>5-x</sub>M<sub>x</sub> system (the Curie temperature *T*<sub>C</sub> for TbNi<sub>5</sub> is 23 K). Several studies have been made on these compounds after replacing Ni with nonmagnetic elements like Al, Ga, Si and Cu [7–10]. These nonmagnetic substitutions lead to a decrease of the Tb 5*d*-band polarization, ordering temperature and magnetic susceptibility. In

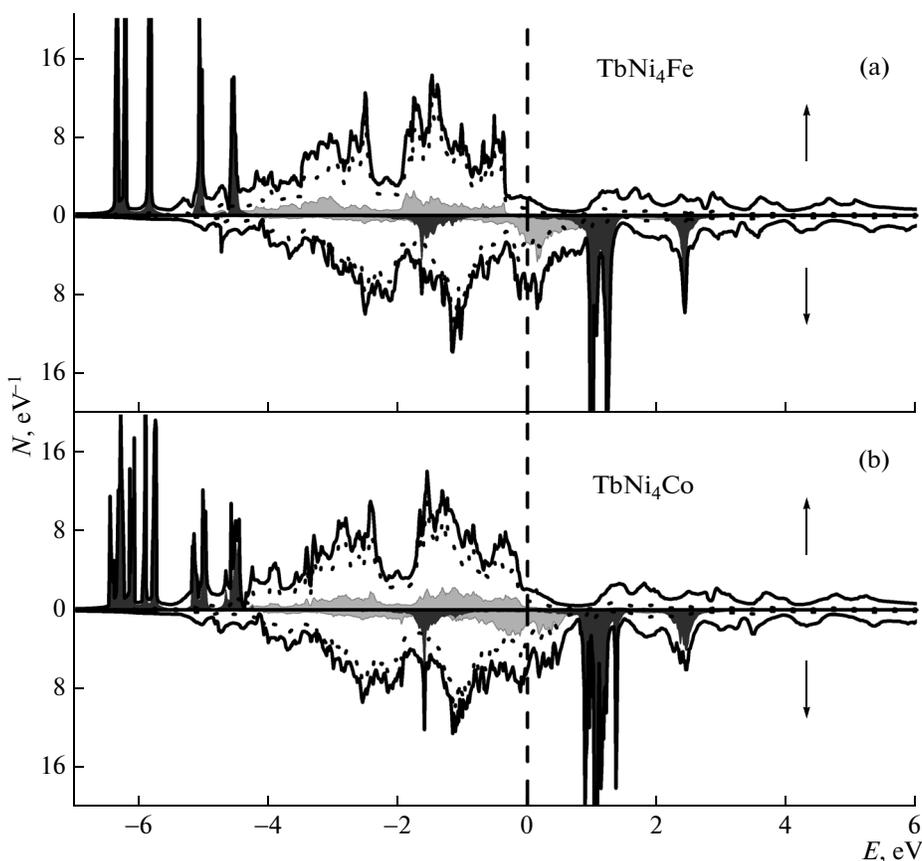
its turn, the replacement of Ni by magnetic Fe or Co ions yields a substantial increase of the Curie temperature in TbNi<sub>4</sub>Co (*T*<sub>C</sub> ~ 60 K) and especially in TbNi<sub>4</sub>Fe (*T*<sub>C</sub> ~ 280 K) [11] that was found to correlate with the enhancement of exchange interaction in the 3*d*-sublattice [12]. Neutron diffraction study has revealed a large magnetic moment 2.3 μ<sub>B</sub> associated with Fe ions occupying only 3*g* positions (in TbNi<sub>4</sub>Fe), while the moment associated with the Co ions that equally occupy 2*c* and 3*g* sites (in TbNi<sub>4</sub>Co) could not be refined [11].

A complex investigation of the energy spectrum and optical properties makes it possible to get the additional information on the influence of the Fe and Co substitutions on the electronic structure of these compounds. Earlier effects of Cu and Al doping on optical conductivity and electronic structure of TbNi<sub>5</sub> have been reported [13, 14]. In this study, in order to investigate the electronic properties of TbNi<sub>4</sub>Fe and TbNi<sub>4</sub>Co, we use the LSDA + *U* calculations and experimental measurements of energy dependences of optical absorption.

## SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Polycrystalline compounds TbNi<sub>4</sub>Fe and TbNi<sub>4</sub>Co were prepared by arc melting of the stoichiometric proportion of the constituent elements of at least 99.9% purity in a water cooled copper hearth in argon atmosphere. The resulting ingots were turned upside down and remelted several times to ensure the homo-

<sup>1</sup> The article is published in the original.



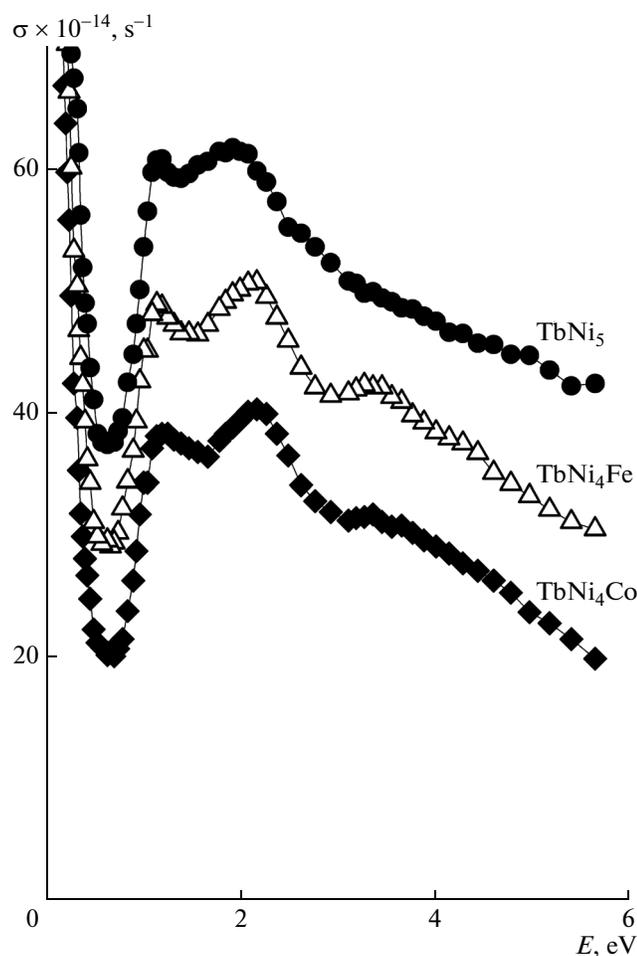
**Fig. 1.** Total electron densities of states (solid curves), partial densities of Tb 4*f*-states (dark regions), Fe and Co 3*d*-states (gray regions) and Ni 3*d*-states (dotted curves) of TbNi<sub>4</sub>Fe (a) and TbNi<sub>4</sub>Co (b). The Fermi energy is at zero energy.

generity. The structural analysis of the samples was performed by room temperature X-ray diffraction patterns, obtained using CuK $\alpha$  radiation. Both compounds are found to crystallize in the hexagonal CaCu<sub>5</sub>-type structure (space group *P6/mmm*) with Tb in 1*a* position (0, 0, 0), two Ni atoms (Ni1) in 2*c* positions (1/3, 2/3, 0) and three Ni atoms (Ni2) in 3*g* positions (1/2, 0, 1/2). Lattice parameters were obtained as  $a = b = 4.9219 \text{ \AA}$ ,  $c = 4.0006 \text{ \AA}$  for TbNi<sub>4</sub>Fe and  $a = b = 4.9026 \text{ \AA}$ ,  $c = 3.9804 \text{ \AA}$  for TbNi<sub>4</sub>Co and these were used in our theoretical calculations.

The spectral measurements were performed at room temperature in the wavelength range of 0.22–15  $\mu\text{m}$  (photon energies 5.64–0.83 eV). The optical constants, i.e., refractive index  $n(\omega)$  and absorption coefficient  $k(\omega)$  ( $\omega$  is the frequency of light wave), were determined by ellipsometric method with a rotating analyzer. Mirror sample surfaces were obtained by means of mechanical polishing with diamond pastes. The values of the optical constants were used to calculate the optical conductivity  $\sigma(\omega) = nk\omega/2\pi$  that is the most sensitive spectral parameter characterizing energy dependence and intensity of optical response.

## ELECTRONIC STRUCTURE CALCULATIONS

The electronic structure calculations were performed self-consistently within the LSDA +  $U$  method (local spin density approximation with Hubbard  $U$ -correction) [15] in the TB-LMTO-ASA package (TB—tight binding, LMTO—linear muffin-tin orbitals, ASA—atomic spheres approximation) [16] for the experimental values of lattice parameters. Electron-electron correlations in the 4*f*-shell of Tb were taken into account with direct  $U = 3.5 \text{ eV}$  and exchange  $J = 0.7 \text{ eV}$  Coulomb interaction parameters as used previously [14]. Spin-orbital coupling was not included in these calculations. We used a  $12 \times 12 \times 12 = 1728$   $k$ -points mesh with 301 irreducible  $k$ -points. Orbital basis included MT-orbitals of the 6*s*-, 6*p*-, 5*d*-, and 4*f*-symmetry for Tb, 4*s*-, 4*p*-, and 3*d*-symmetry for Ni, Co, and Fe. MT-radius for Tb was 3.49 a. u., for Ni, Fe, and Co in both positions—2.64 a. u. A ferromagnetic ordering of all magnetic moments was obtained in the calculations in agreement with experimental data [11]. The calculated moments of Tb in both compounds were found as 6  $\mu_B$ , and up to 0.3  $\mu_B$  for Ni ions in both positions. At the same time, in our calculations the moment of Fe was found as 2.4  $\mu_B$ , the Co ions as 1.23  $\mu_B$  in 2*c* position and 1.1  $\mu_B$  in 3*g* position.



**Fig. 2.** Experimental spectra of optical conductivities of  $\text{TbNi}_4\text{Fe}$  (triangles) and  $\text{TbNi}_4\text{Co}$  (diamonds) compounds. Also optical conductivity of  $\text{TbNi}_5$  [14] is shown for comparison. Each curve is shifted upwards by 10 units.

Total densities of states  $N(E)$  of  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  are shown in two panels of Fig. 1 for both opposite spin directions ( $\uparrow$ ) and ( $\downarrow$ ) together with the partial  $4f$ -states of Tb and  $3d$ -states of Ni and Fe(Co). One can see that in  $N(E)$  of  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  just below the Fermi energy ( $E_F$ ) down to  $-5$  eV, there is a broad band of Ni  $3d$ -states. In the spin-up  $\uparrow$  system Tb  $4f_1$ -electronic states are located within  $4.5$ – $7$  eV below the Fermi level, intensive  $4f_1$ -peaks are placed at  $1.5$  and  $2$  eV above it. The structure of the Ni  $3d$ -states is characterized by a small splitting between two spin directions. In  $\text{TbNi}_4\text{Fe}$ , the Fe  $3d$ -states hybridize with the other states and contribute to a broad energy range with substantial spin splitting following the large value of the Fe moment. Similar partial density of states for Co can be found in  $\text{TbNi}_4\text{Co}$ . The Co-substitution in  $2c$  position gives rise to a larger magnetic moment that corresponds to the electronic states in the spin-down  $\downarrow$  system just above the Fermi level up

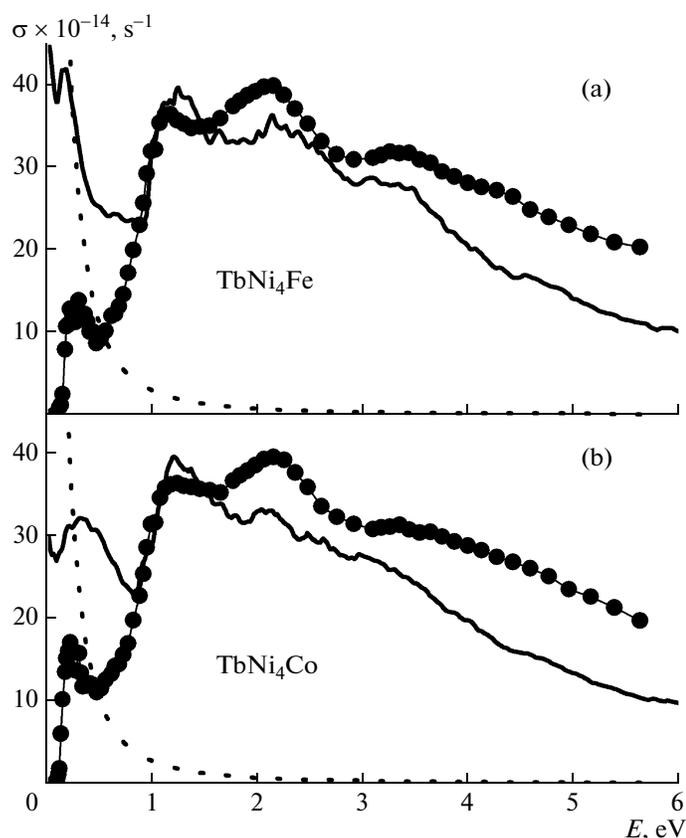
to  $1$  eV. While a moderate spin splitting is seen in the case of Co  $3g$  substitution that makes partial Ni  $3d$ -density of states of both  $2c$  and  $3g$  positions almost comparable in magnitude in the whole energy range.

Although the behavior of total  $N(E)$  for  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  on the whole is similar to that of  $\text{TbNi}_5$  [14], some essential distinctions are noteworthy. As Fe or Co substitute for Ni, the  $N(E)$  curves exhibit transformations both near the Fermi level and in the energy range below  $E_F$  down to  $-4$  eV. Moreover some maxima are shifted from  $E_F$  and their intensities are substantially different. Note also that the broad distribution character of Fe and Co impurity bands in the  $N(E)$  of these compounds is radically different from the localized Cu-band in the  $\text{TbNi}_{5-x}\text{Cu}_x$  system [13], which exhibits a significant maximum in the density of states near  $4$  eV below the  $E_F$ .

## RESULTS AND DISCUSSIONS

Figure 2 shows the spectra of optical conductivity  $\sigma(\omega)$  for  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  compounds (the curves are shifted along the ordinate axis by 10 units). For comparison, the figure also shows the  $\sigma(\omega)$  dependence for the parent  $\text{TbNi}_5$  [14]. At low energies the behavior of the optical conductivities for all compounds is determined by an abrupt decrease which is typical for Drude absorption of electromagnetic waves ( $\sigma \sim \omega^{-2}$ ). As the light frequency increases ( $\hbar\omega > 0.8$  eV), the character of the  $\sigma(\omega)$  dependences indicates the dominant role of quantum transitions. The energy range related to interband absorption contains a number of features, whose location and intensity are affected by the compound composition. In the spectrum  $\sigma(\omega)$  of binary compound  $\text{TbNi}_5$ , two pronounced peaks are observed at energies of  $1.1$  and  $1.9$  eV. With the replacement of Ni with Fe or Co atoms, these peaks remain nearly invariable and the new maximum at  $\sim 3.4$  eV appears in the optical conductivities of ternary systems.

In Fig. 3 the interband parts of the measured and the calculated optical conductivities of  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  compounds are shown. The experimental curves were obtained as  $\sigma_{\text{ib}} = \sigma - \sigma_D$ , where  $\sigma_D$  is the Drude term (dotted curves). Its dispersion was determined using plasma ( $\omega_p$ ) and relaxation ( $\gamma$ ) frequencies of free charge carriers ( $\omega_p = 6.5 \times 10^{-15} \text{ s}^{-1}$ ,  $\gamma = 21 \times 10^{-14} \text{ s}^{-1}$  for  $\text{TbNi}_4\text{Fe}$  and  $\omega_p = 6.1 \times 10^{-15} \text{ s}^{-1}$ ,  $\gamma = 22 \times 10^{-14} \text{ s}^{-1}$  for  $\text{TbNi}_4\text{Co}$ ) calculated in the infrared range. One can see that the interband optical conductivity spectra of these alloys are rather similar to each other and reveal a group of interband absorption peaks of the same nature—three strong maxima in the visible and ultraviolet regions and the smaller peak in the infrared part of the spectrum.



**Fig. 3.** Interband optical conductivity spectra of  $\text{TbNi}_4\text{Fe}$  (a) and  $\text{TbNi}_4\text{Co}$  (b). Circles represent the experimental data, the solid curves—calculated optical conductivity. The dotted line corresponds to the Drude term contribution.

The electronic densities  $N(E)$  for the spin-up and spin-down states, shown in Fig. 1, were used to interpret the experimental data. In general, the interband absorption represents a superposition of contributions from energy bands with  $\uparrow$ - and  $\downarrow$ -electrons. The structures of  $N(E)$  for the investigated compounds point out at nearly equivalent contributions to the optical absorption from each spin direction because of the similarity of the Ni  $d_{\uparrow}$ - and Ni  $d_{\downarrow}$ -band structures. In the  $\downarrow$ -systems the transitions with the participation of  $f$ -electrons is also present in this spectral region. The interband optical conductivities (shown in figures in arbitrary units) were calculated according to [17] directly from the calculated electronic structure through the convolution of the total  $N(E)$  both below and above  $E_F$  in assuming that the direct and indirect transitions are equally probable. The curves  $\sigma_{\text{ib}}$  for both compounds predict a strong absorption region up to  $\sim 6$  eV, formed by electron transitions between the states with the larger values of the total  $N(E)$ . In the calculated spectra  $\sigma_{\text{ib}}$  three pronounced peaks are observed at energies near 0.3; 1.2–1.5 and 2.2–2.5 eV. The presence of these intense absorption structures for

$\hbar\omega < 3$  eV according to the calculated  $N(E)$  can be related mainly to the electronic transitions between the hybridized  $d$ -bands of Ni. The calculations also predict appearance of wide maxima in  $\sigma_{\text{ib}}$  curves for  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  in the range of 3–4 eV, which was not observed earlier in the optical conductivity study of  $\text{TbNi}_5$  [14]. Thus it is clear that the observed peculiarity is typical only for ternary compounds and arises due to the redistribution of electronic density of parent compound upon replacing Ni by Fe or Co.

A comparison of the experimental interband optical conductivity with the theoretical ones shows their certain similarity with respect to the position of the main maxima and the same energy range of quantum absorption. On the whole, observed frequency dependences of  $\sigma_{\text{ib}}$  for the investigated compounds are satisfactorily described within ab initio spin-resolved calculations of the electronic structure obtained by LSDA +  $U$  method.

## CONCLUSIONS

In this paper, the optical conductivity and electronic structure of  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  were investigated in order to reveal their characteristic features in comparison with the parent compound  $\text{TbNi}_5$ . The spectral properties were measured by ellipsometric method in the wavelength range of 0.22–15  $\mu\text{m}$ . The electronic structure of  $\text{TbNi}_4\text{Fe}$  and  $\text{TbNi}_4\text{Co}$  was calculated within the LSDA +  $U$  method (local spin density approximation with Hubbard  $U$ -correction). Based on the calculated electronic structure results, a theoretical optical conductivity was calculated and used to interpret the experimental conductivity in the range of interband optical absorption.

## ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, research project No. 13-02-00256, the grant of the Ministry of education and science of Russian Federation, project No. 14.A18.21.0076, the scientific program “Development of scientific potential of universities,” the Dynasty Foundation.

## REFERENCES

1. E. Trémolet de Lacheisserie, D. Gignoux, M. Schlenker, *Magnetism: Materials and Applications* (Springer, Berlin, 2005).
2. K. A. Gschneidner, V. K. Pecharsky, and A. O. Tsokol, *Rep. Progr. Phys.* **68**, 1479 (2005).
3. N. V. Mushnikov, *Phys. Uspekhi* **55**, 421 (2012).
4. J. M. D. Coey, *Magn. IEEE Trans.* **47**, 4671 (2011).
5. A. G. Kuchin, A. S. Ermolenko, Yu. A. Kulikov, V. I. Khrabrov, E. V. Rosenfeld, G. M. Makarova, T. P. Lapina, and Ye. V. Belozarov, *J. Magn. Mater.* **303**, 119 (2006).

6. A. Bajorek, G. Chelkowska, and B. Andrzejewski, *J. Alloys Comp.* **509**, 578 (2011).
7. E. Burzo, A. Takács, M. Neumann, and L. Chioncel, *Phys. Stat. Sol. (c)* **1**, 3343 (2004).
8. R. Lizárraga, A. Bergman, T. Björkman, H. P. Liu, Y. Andersson, T. Gustafsson, A. G. Kuchin, A. S. Ermolenko, L. Nordström, and O. Eriksson, *Phys. Rev. B* **74**, 094419 (2006).
9. M. Falkowski, B. Andrzejewski, and A. Kowalczyk, *J. Alloys Comp.* **442**, 155 (2007).
10. D. A. Joshi, C. V. Tomy, D. S. Rana, R. Nagarajan, and S. K. Malik, *Solid State Commun.* **137**, 225 (2006).
11. A. Haldar, I. Dhiman, A. Das, K. G. Suresh, and A. K. Nigam, *J. Alloys Comp.* **509**, 3760 (2011).
12. A. V. Lukoyanov, A. Haldar, A. Das, A. K. Nayak, K. G. Suresh, and A. K. Nigam, *J. Appl. Phys.* **109**, 07E152 (2011).
13. I. A. Nekrasov, E. E. Kokorina, V. A. Galkin, Yu. I. Kuz'min, Yu. V. Knyazev, and A. G. Kuchin, *Physica B* **407**, 3600 (2012).
14. Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuz'min, and A. G. Kuchin, *Phys. Solid St.* **55**, 385 (2013).
15. V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).
16. O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
17. C. N. Berglund and W. E. Spicer, *Phys. Rev.* **136**, 1044 (1964).