ISSN 0031-918X, Physics of Metals and Metallography, 2018, Vol. 119, No. 13, pp. 1254–1258. © Pleiades Publishing, Ltd., 2018.

THEORY
OF METALS

Electronic Structure and Magnetic Properties of Strongly Correlated Transition Metal Compounds[1]

V. I. Anisimov[a, b, *], **A. V. Lukoyanov**[a, b], **and S. L. Skornyakov**[a, b]

[a] *Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Ekaterinburg, 620108 Russia*
[b] *Ural Federal University Named after the First President of Russia B.N. Yeltsin, Ekaterinburg, 620002 Russia*
**e-mail: via@imp.uran.ru*

Received March 26, 2018

Abstract—Different classes of compounds based on transition metals belong to strongly correlated compounds due to strong interactions of *d* and *f* electrons with each other and with itinerant electronic states. This results in a number of interesting phenomena, including metal–insulator and various magnetic spin transitions, "heavy fermion" compounds, interplay between magnetic order and superconductivity, formation of local magnetic moments, anomalies of transport properties, etc. Recent results in this field based on applications of ab initio approaches and dynamical mean-field theory are reviewed in this paper.

Keywords: electronic structure, strongly correlated compounds, optical properties

DOI: 10.1134/S0031918X18130161

INTRODUCTION

The richness of physical phenomena of transition metal *d* and *f* compounds brings them to the cutting edge of experimental and theoretical studies, capturing the attention of researchers for a great variety of interesting phenomena: magnetic spin transitions, metal-insulator transitions, "heavy fermion" behavior, interplay between magnetic order and superconductivity, appearance and disappearance of local magnetic moments, and anomalies of transport properties [1–6]. Strong interactions of *d* and *f* electrons with each other and with itinerant electrons are responsible for anomalous properties of compounds. Electronic structure calculations for strongly correlated materials should explicitly take into account Coulomb interactions between *d* or *f* electrons. Recent advances in this field are related to the development of the LDA + DMFT method, which combines local density approximation (LDA) [7] with dynamical mean-field theory (DMFT). The problem defined by Hamiltonian can be solved in static mean-field approximation. This calculation scheme is called the LDA + U method. This method was found to be very successful when applied to the systems with long-range spin and orbital orders. Recently this approach was extended to account for spin-orbit coupling [8]. However, the more general problems of paramagnetic insulators and strongly correlated metals can be solved only by the DMFT method [9]. The approach based on the DMFT solution of the problem defined by the Hamiltonian with the DFT-calculated parameters is called the DFT + DMFT method [10].

CALCULATION DETAILS

In this work we review studies carried out in different computational packages, based on DFT and DFT + DMFT methods. We start with the results obtained within the AMULET package—Advanced Materials simULation Ekaterinburg's Toolbox [11]. Various branches of this code were actively tested for different problems and systems such as NiO, $KCuF_3$, FeS, etc. The other computational methods were also employed [8].

RESULTS AND DISCUSSION

In the framework of the DFT + DMFT method, spin transitions in the $FeSiO_3$ clinoferrosilite under pressure were obtained. It was found that iron ions in $FeSiO_3$ undergo two spin transitions from high-spin to low-spin state: at 1200 K, transitions occur at 100 and 120 GPa, passing completely to the low-spin state at 120 and 150 GPa, respectively. At higher temperatures, the boundaries of the spin transitions and pressures increase. For $FeSiO_3$ iron ions, an estimate was made of the energy levels of atomic orbitals for all pressure values, and the probability of electronic configurations was calculated, which made it possible to establish that the spin crossover consists predominantly of the high and low-spin configurations coexisting in the transition region. The obtained results allow us to

---

[1] The article is published in the original.

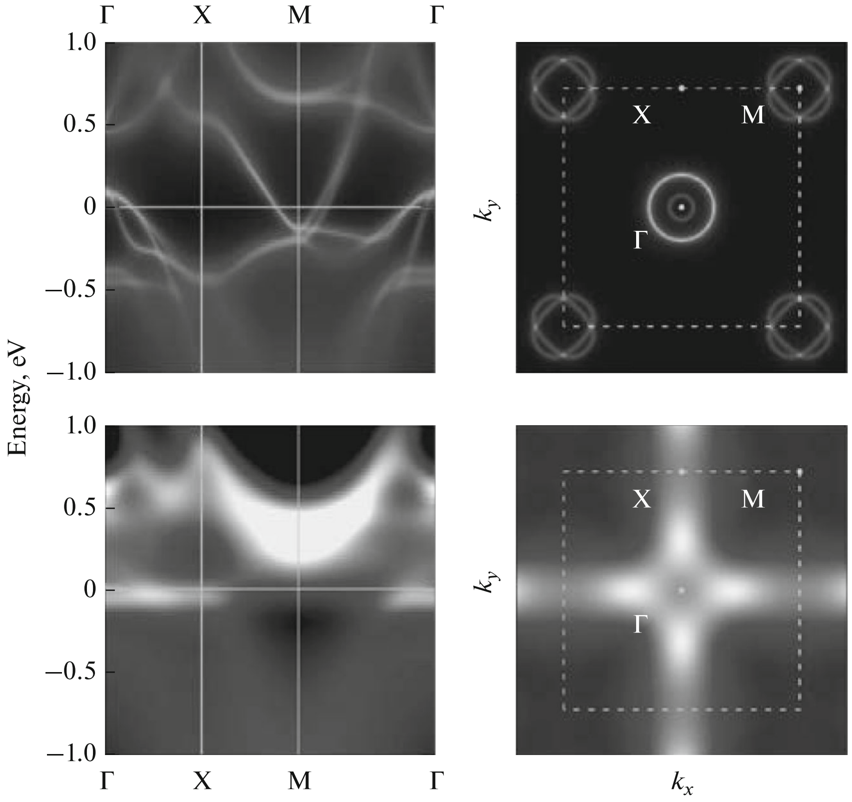

Fig. 1. Electronic structure (left column) and Fermi surface (right column) of paramagnetic FeSe in the Γ–X–M plane of the reciprocal space as obtained using the DFT + DMFT method at $T = 390$ K. Top row shows the results for the lattice constant $a = 7.05$ a.u. (low volume). Bottom row corresponds to $a = 7.6$ a.u. (high volume).

expand our understanding of the magnetic properties of the minerals of the lower Earth mantle [12].

In a similar $FeBO_3$ compound, the magnetic properties and electronic structure under pressure were studied. It was found that the iron borate undergoes a collapse of the magnetic moment and a spin transition under pressure accompanied by an isostructural transition. The resulting volume collapse is 13%. As a result of the spin transition under pressure, the conductivity gap decreases from about 3 to 0.5 eV [13].

Employing the fully charge self-consistent implementation of the method, combining density functional theory and dynamical mean-field theory the study of the effect of electron correlations on the elastic, spectral and magnetic properties of the prototypical iron-based chalcogenide superconductor FeSe was carried out. Iron selenide crystallizes in the same layered structure as the pnictide iron-based superconductors, containing layers of edge-sharing $FeSe_4$ tetrahedra, but without separating (nonconducting) layers. Therefore FeSe is regarded as the parent compound of Fe-based superconductors which represents a minimal model material for understanding the mechanism of superconductivity of FeSCs.

In our calculations we showed that the structural and magnetic anomalies induced by the lattice expansion both in the paramagnetic and magnetically ordered phases can be explained within a unified mechanism. It has been predicted that the electronic structure of FeSe undergoes a remarkable change accompanied by a complete reconstruction of the Fermi surface (Lifshitz transition) upon a moderate expansion of the lattice volume (negative chemical pressure). In particular, we found that upon expansion of the lattice the spectral weight of the electron pockets centered at the M point vanishes. The hole pocket encircling the Γ point transforms into a large square-like Fermi surface surrounding the M point with the four pronounced spots around the Γ point. Thus, the transition is characterized by a change of the nesting wave vector from (π, π) to (π, 0) (Fig. 1, right panels). The observed topological change proceeds similarly to the evolution of the experimental photoemission spectra of the doped $FeSe_{1-x}Te_x$ samples. The experiment confirms the emergence of the Fermi surface pocket at the X point for large concentrations of Te for $x > 0.7$. We demonstrated that this behavior can be attributed to a correlation-induced shift of the Van Hove singularity of the Fe t_2 bands at the M point across the

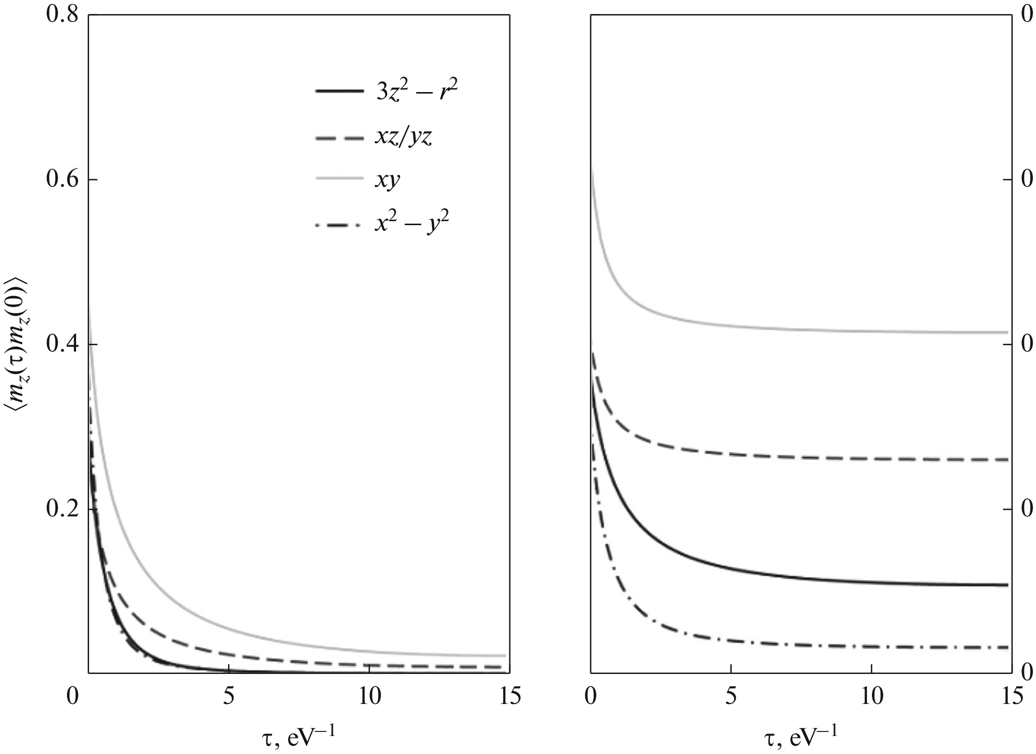

Fig. 2. Orbitally resolved local spin correlation functions $\chi(\tau) = \langle m_z(\tau)m_z(0)\rangle$ of paramagnetic FeSe calculated using the charge-self-consistent DFT + DMFT at $T = 390$ K for the lattice constant $a = 7.05$ a.u. (left) and $a = 7.60$ a.u. (right).

Fermi level (Fig. 1, left panels). In particular, we find that upon expansion of the lattice a substantial part of the spectral weight in the vicinity of E_F at the M point is pushed from below to above the Fermi level, while the position of the energy bands near the Γ point remains unaffected.

We show that the transition in the electronic structure is associated with a crossover from itinerant to localized magnetic moments as is seen from the spin correlation function (Fig. 2). This behavior is consistent with the coherence-incoherence transition scenario which was found experimentally in the Fe(Se,Te) series. Our calculations revealed a strong orbital selectivity in the formation of the local moments upon expansion of the lattice of FeSe. In particular we show that the *xy* orbital plays a predominant role, while the contribution of the *xz*/*yz* orbitals is substantially weaker. On the other hand, the *e* orbitals exhibit an itinerant moment behavior.

It has been obtained that the in-plane ($q_z = 0$) momentum-dependent static spin susceptibility $\chi(q)$ shows a maximum at the corners of the tetragonal Brilloiun zone at the M points for the equilibrium volume. This confirms that the leading magnetic instability of FeSe at ambient pressure occurs at the wave vector (π, π), in agreement with experiment. An expansion of the lattice volume leads to a suppression of the maximum at (π, π) and the development of a maximum at (π, 0). This change of the magnetic correlations proceeds in agreement with the change of the Fermi surface and is associated with the change of the nesting vector. The calculated evolution of $\chi(q)$ qualitatively agrees with the experimentally observed transformation of magnetic correlations in the Fe(Se,Te) series.

Thus, we propose that the anomalous behavior of FeSe upon expansion is connected with the proximity of the Fe t_2 Van Hove singularity to the Fermi level and the sensitive dependence of its position on external conditions [14, 15].

Properties of the intermetallic compounds of *d* and *f* metals were also studied. The evolution of the electronic structure of NpMT$_5$ (M – 3*d* and 4*d* metals, T = Ga, In) compounds was investigated [16]. Both strong electronic correlations and spin-orbit coupling in the 5*f* shell of neptunium were taken into account. The analysis of the calculated electronic structure and characteristics of 5*f* ions similar to [17] showed that in NpMIn$_5$ for M = Fe, Co, Ni, the neptunium ions are found to be characterized by the electron configuration closer to f^4.

Investigations of the electronic, magnetic, and optical properties of triple compounds of rare-earth and transition metal are of interest for practical use. In

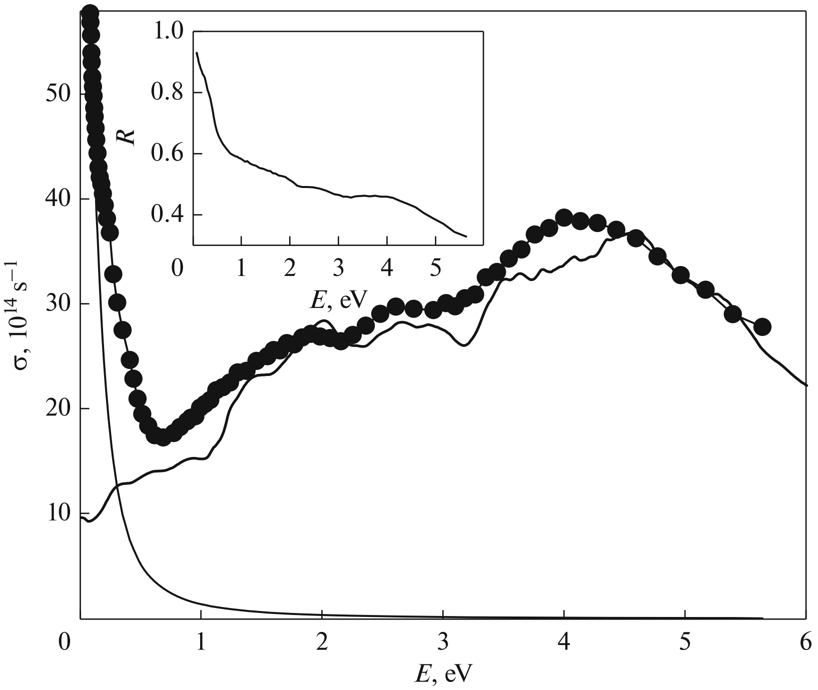

Fig. 3. Theoretical (solid curve) and experimental (dots) optical conductivity of $TbNiGe_2$, the inset shows the reflectivity.

$TbNiGe_2$ the magnetocaloric effect was found [18]. For $TbNiGe_2$ and $RAgSn_2$ (R = Ho, Er), theoretical studies of the electronic structure and magnetic state were done within LSDA + U to account antiferromagnetic long-range ordering. Also magnetic and optical characteristics were measured [18].

The theoretical optical conductivity was compared with the experimental results, taking into account the Drude contribution (see Fig. 3). The correction for strong electron-electron interactions in the 4*f* shell of R in our calculations resulted in a very good agreement with experimental data [19, 20].

CONCLUSIONS

Thus, in this paper recent results obtained for different classes of transition metal compounds are reviewed. Recent progress in this field based on applications of ab initio approaches and dynamical mean-field theory is reviewed in this paper. For clinoferrosilite $FeSiO_3$ under pressure the spin transitions were obtained. The volume collapse of 13% was reproduced in $FeBO_3$. In prototypical iron-based superconductor FeSe an anomalous behavior of structural, spectral and magnetic properties triggered by electronic correlation was demonstrated. For $NpMIn_5$ (M = Fe, Co, Ni) and $TbNiGe_2$ compounds the electronic structure and magnetic properties were investigated. All the reviewed results show recent advances of computational methods to successfully investigate different properties of strongly correlated transition metal compounds.

ACKNOWLEDGMENTS

The research was carried out within the state assignment of FASO of Russia (theme Electron AAAA-A18-118020190098-5).

REFERENCES

1. J. M. Rondinelli, K. R. Poeppelmeier, and A. Zunger, "Research Update: Towards designed functionalities in oxide-based electronic materials," APL Mater. **3**, 080702 (2015).
2. V. I. Anisimov, V. V. Dremov, M. A. Korotin, G. N. Rykovanov, and V. V. Ustinov, "First principles electronic structure calculation and simulation of the evolution of radiation defects in plutonium by the density functional theory and the molecular dynamics approach," Phys. Met. Metallogr. **114**, 1087–1122 (2013).
3. M. A. Korotin, Z. V. Pchelkina, N. A. Skorikov, A. V. Efremov, and V. I. Anisimov, "Electronic structure of $UO_{2.12}$ calculated in the coherent potential approximation taking into account strong electron correlations and spin-orbit coupling," Phys. Met. Metallogr. **117**, 655–664 (2016).
4. R. Arita, K. Kuroki, K. Held, A. V. Lukoyanov, S. Skornyakov, and V. I. Anisimov, "Origin of large thermopower in $LiRh_2O_4$: Calculation of the Seebeck coefficient of local density approximation and dynamical mean-field theory," Phys. Rev. B **78**, 115121 (2008).

5. E. I. Shreder, A. A. Makhnev, A. V. Lukoyanov, and K. G. Suresh, “Optical properties and the electron structure of Co_2TiGe and Co_2TiSn Heusler alloys,” Phys. Met. Metallogr. **118**, 965–969 (2017).
6. M. R. Norman, “Materials design for new superconductors,” Rep. Prog. Phys. **79**, 074502 (2016).
7. R. O. Jones, “Density functional theory: Its origins, rise to prominence, and future,” Rev. Mod. Phys. **87**, 897–923 (2015).
8. A. O. Shorikov, A. V. Lukoyanov, M. A. Korotin, and V. I. Anisimov, “Magnetic state and electronic structure of the delta and alpha phases of metallic Pu and its compounds,” Phys. Rev. B **72**, 024458 (2005).
9. G. Kotliar and D. Vollhardt, “Strongly correlated materials: Insights from dynamical mean-field theory,” Phys. Today **57**, 53–59 (2004).
10. V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, “First-principles calculations of the electronic structure and spectra of strongly correlated systems: Dynamical mean-field theory,” J. Phys.: Condens. Matter **9**, 7359–7368 (1997).
11. http://www.amulet-code.org.
12. A. A. Dyachenko, A. O. Shorikov, A. V. Lukoyanov, and V. I. Anisimov, “Two successive spin transitions in a wide range of pressure and coexistence of high- and low-spin states in clinoferrosilite $FeSiO_3$,” Phys. Rev. B **93**, 245121 (2016).
13. A. A. Dyachenko, A. O. Shorikov, and V. I. Anisimov, “Phase transitions in $FeBO_3$ under pressure: DFT+DMFT study”, JETP Lett. **106**, 317–323 (2017).
14. S. L. Skornyakov, V. I. Anisimov, D. Vollhardt, and I. Leonov, “Effect of electron correlations on the electronic structure and phase stability of FeSe upon lattice expansion,” Phys. Rev. B **96**, 035137 (2017).
15. S. L. Skornyakov, I. Leonov, and V. I. Anisimov, “Effect of magnetic order on the phase stability of the parent chalcogenide compound FeSe,” JETP Lett. **103**, 265–268 (2016).
16. A. V. Lukoyanov, A. O. Shorikov, and V. I. Anisimov, “Electronic structure of the $NpMT_5$ (M = Fe, Co, Ni; T = Ga, In) series of neptunium compounds,” Phys. Solid State **58**, 438–443 (2016).
17. A. V. Lukoyanov and V. I. Anisimov, “Electronic structure of nitrides PuN and UN,” J. Exp. Theor. Phys. **123**, 864–868 (2016).
18. S. Gupta, K. G. Suresh, A. V. Lukoyanov, Yu. V. Knyazev, Yu. I. Kuz’min, “Magnetism, electronic structure and optical properties of $TbNiGe_2$,” J. Alloys Compd. **664**, 120–124 (2016).
19. Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuz’min, S. Gupta, and K. G. Suresh, “Electronic structure of the $TbMn_{0.33}Ge_2$ compound: Band calculation and optical experiment,” Phys. Solid State **58**, 2373–2378 (2016).
20. S. Gupta, K. G Suresh, A. V. Lukoyanov, Yu. V. Knyazev, and Yu. I. Kuz’min, “Theoretical and experimental investigations on the magnetic and related properties of $RAgSn_2$ (R = Ho, Er) compounds,” J. Mater. Sci. **51**, 6341–6347 (2016).