

## Electron correlation effects in band structure of magnetic clusters $Mn_{12}$ and $Fe_8$

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### Abstract

We present calculations of electronic structure and local magnetic moment of 3d metals in  $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{24}] \cdot 2CH_3COOH \cdot 4H_2O$  and  $[(C_6H_{15}N_3)_6Fe_8O_2(OH)_{12}]Br_7(H_2O)Br \cdot 8H_2O$ , abbreviated  $Mn_{12}$  and  $Fe_8Br_8$ , respectively. The comparison of calculated and experimental soft X-ray spectra shows that p–d mixing is very sensitive to the value of the local Coulomb repulsion parameter  $U$ . This result is found to be in agreement with experimental resonant inelastic X-ray scattering spectra (RIXS) and X-ray photoelectron spectra (XPS), which have been used to study electron correlation effects in magnetic clusters. The O 2p–Me 3d separation found in the experiment, is well reproduced by LDA +  $U$  band structure calculations, which include on-site Coulomb interactions. The 3d metal  $L_{2,3}$  RIXS behaviour reflects the presence of the local magnetic moment and confirms the existence of the energy gap in the 3d band of the metal.

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### 1. Introduction

Magnetic molecular clusters, formed by a large number of strongly interacting metal ions, have attracted much attention during recent years as nanometer-sized single-domain magnetic particles with a high-spin ground state [1,2]. Among the molecules belonging to this family,  $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{24}] \cdot 2CH_3COOH \cdot 4H_2O$  and  $[(C_6H_{15}N_3)_6Fe_8O_2(OH)_{12}]Br_7(H_2O)Br \cdot 8H_2O$ , from here on abbreviated  $Mn_{12}$  and  $Fe_8Br_8$ , respectively, are the most intensely studied systems having magnetic properties on a molecular scale. Since the symmetry at the magnetic ions in such clusters is usually low because of multidentate ligands in the system, the orbital degeneracy would be lifted thus leading to weaker ferromagnetic-exchange interactions. One

therefore should expect low-spin ground states in these systems. To study the magnetization behavior of the cluster under the influence of externally applied magnetic fields, it is necessary to assemble an accurate model Hamiltonian. The low-lying states in magnetic cluster can be determined by exact diagonalization the corresponding exchange Hamiltonian. Accurate electronic structure calculations are necessary to realize this because the exchange constants are very sensitive to the ordering of energy levels. First-principles electronic structure calculations are very difficult or almost impossible to perform for such clusters for a number of reasons. First, the computational limitations allow calculating clusters only with limited sizes. The next problem is electron correlation effects, which usually are present in transition metal oxide systems and cannot be described properly in a conventional local density approach (LDA) (see [3]). The application of LDA +  $U$  (see [4]) presents a solution of this problem to some extent and describes opening of the band

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gap as well as correct values for local magnetic moments. The obtained results are sensitive to the choice of the on-site Coulomb repulsion parameterized by the value of  $U$ . In our previous publications devoted to the electronic structure of transition metal compounds we have shown that the selection of parameter  $U$  can be somewhat obtained from comparing LDA +  $U$  calculations with X-ray emission (XES) and X-ray photoelectron measurements [5,6]. In the present study of electronic structure of  $Mn_{12}$  and  $Fe_8Br_8$ , we follow the same approach. LDA +  $U$  calculations of these magnetic clusters are performed for different values of  $U$  and the comparison of calculation and experiment allows determining  $U$ .

Soft X-ray fluorescence spectroscopy is a powerful tool for studying the electronic structure of solids. The technique has a number of advantages, some of which have been found to be especially important when applied to magnetic clusters. XES probes the bulk electronic properties of materials due to its relatively large penetration and escape depth of the respective incident and emitted photons. Secondly, XES allows determining the local *partial* density of occupied states, both element-specific and angular-momentum selective. In combination with X-ray photoelectron valence band spectra (XPS VB), which probe the *total* density of occupied states, one can receive full information about the electronic structure of multi-component compounds, such as magnetic clusters, which then can be directly compared to band structure calculations.

Here we use the resonant inelastic X-ray scattering (RIXS) to estimate the magnitude of the local magnetic moment and the degree of spin-polarization of the 3d band of the metal. According to previous observations [7,13], the large local magnetic moment leads to an increase in the intensity ratio of the  $L_2$  and  $L_3$  fluorescence peaks,  $I(L_2)/I(L_3)$ , while the presence of the energy gap affects the 3d metal  $L_3$  resonant X-ray emission spectra (XES).

## 2. Experimental and calculational details

The XPS measurements were carried out with a PHI 5600 ci multi-technique spectrometer using monochromatized Al  $K\alpha$  radiation ( $E_{exc} = 1486.6$  eV). The estimated energy resolution consists is 0.35 eV and the base pressure in the vacuum chamber during the measurements was about  $5 \times 10^{-9}$  Torr. The 3d metal (Mn and Fe)  $L_{2,3}$  ( $3d_{4s} \rightarrow 2p_{1/2,3/2}$  transitions), carbon, nitrogen and oxygen  $K\alpha$  ( $2p \rightarrow 1s$  transition) XES were recorded at the soft X-ray spectroscopy endstation on Undulator Beamline 8.0 at the Advanced Light Source located at Lawrence Berkeley National Laboratory. The 3d metal  $L_{2,3}$  XES were measured resonantly through the iron  $L_{2,3}$  edges. The carbon, nitrogen and oxygen  $K\alpha$  XES were recorded non-resonantly (far above threshold). The energy resolution of the 3d-metal  $L_{2,3}$  XES, carbon, nitrogen and oxygen  $K$  XES is about 0.8, 0.3, 0.4 and 0.4 eV, respectively. The resonant 3d metal  $L_{2,3}$  XES are normalized to the number of incoming photons monitored

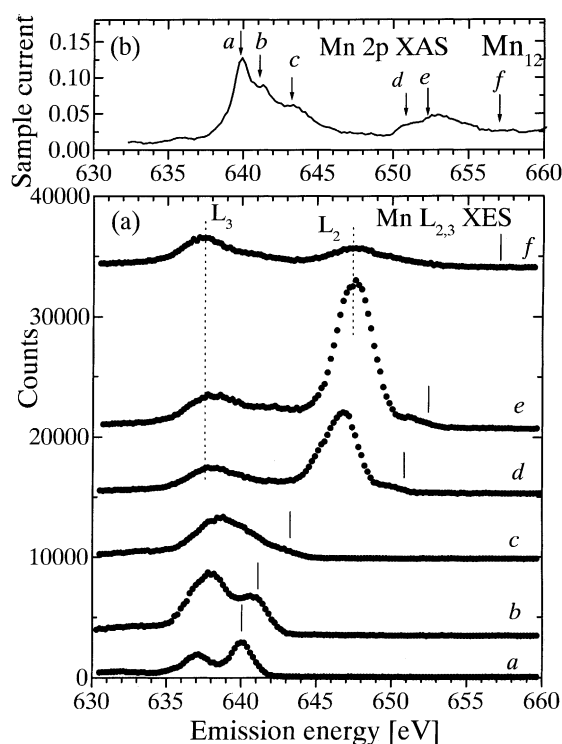


Fig. 1. Excitation energy dependence of 3d-metal  $L_{2,3}$  XES of  $Mn_{12}$ . Upper panel is Mn 2p XAS measured in total electron yield mode. The lower panel is Mn  $L_{2,3}$  XES resonantly excited at energies a–f corresponding to selected features on Mn 2p XAS.

by a gold mesh current. The 3d metal 2p X-ray absorption spectra were measured in total electron yield (TEY) mode.

The electronic structure calculations were performed for molecules of  $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{24}] \cdot 2CH_3COOH \cdot 4H_2O$  and  $[(C_6H_{15}N_3)_6Fe_8O_2(OH)_{12}]Br_7(H_2O)Br \cdot 8H_2O$  except only water of crystallization. The spin polarized LDA +  $U$  approach is described in [6] in detail. The detailed band structure calculations of  $Mn_{12}$  and  $Fe_8Br_8$ -clusters have been carried for three values of  $U$  of 0, 4 and 8 eV, keeping the value of the intra-atomic Hund's exchange parameter constant ( $J = 0.9$  eV).

## 3. Results and discussion

In the case of 3d-metal compounds, the study of the occupied 3d-states with non-resonant  $L_{2,3}$  XES is rather complicated because  $L_3$  ( $3d_{4s} \rightarrow 2p_{3/2}$ ) and  $L_2$  ( $3d_{4s} \rightarrow 2p_{1/2}$ ) X-ray transitions are overlapped. To overcome this difficulty the resonant excitation of  $L_{2,3}$  XES is used where the energy of incoming photons is tuned near 2p-thresholds which provides the selective excitation of  $L_3$  XES.

Figs. 1 and 2 show  $L_{2,3}$  fluorescence of the transition metal for  $Mn_{12}$  and  $Fe_8Br_8$  resonantly excited through the 2p threshold. The excitation energies are selected in accordance with spectral features present in the 2p absorption of the 3d-metal (upper panels of Figs. 1 and 2). The excitation energies are represented by vertical lines in the emission

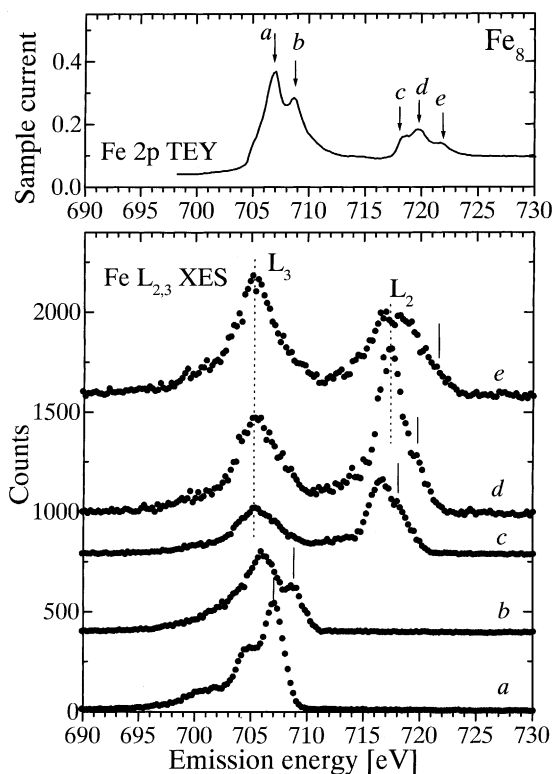


Fig. 2. Excitation energy dependence of 3d-metal  $L_{2,3}$  XES of  $Fe_8Br_8$ . Upper panel is Fe p XAS measured in total electron yield mode. The lower panel is  $Fe_{L_{2,3}}$  XES resonantly excited at energies a–f corresponding to selected features on Fe 2p XAS.

spectra and correspond to the energy of the elastic peaks. For the  $L_{2,3}$  spectra obtained far from  $2p_{1/2}$  excitation energy, the  $I(L_2)/I(L_3)$  ratio of Mn, Fe spectra is about 0.59 and 0.65, respectively. This allows to estimate the local magnetic moment to be in the range of 3–4  $\mu_B$  (see [7,10,13]). When exciting below the  $L_2$  absorption edge we probe the Mn  $L_3$  and Fe  $L_3$  fluorescence spectra. It has been shown that the unoccupied states can participate in formation of  $L_{2,3}$  in X-ray emission transitions [12] indicating the presence of an energy gap in magnetic materials, which we adopted for the  $Mn_{12}$  and  $Fe_8Br_8$  magnetic clusters.

The selectively excited 3d-metal  $L_3$  XES are overlapping with the weak elastic peaks but the unoccupied 3d-states still can be derived [11]. The  $L_3$  spectra behavior is the same as, for example, Cr  $L_3$ , which is half-metallic with a strongly spin-polarized Cr 3d band [12] indicating rather small energy gap in  $Mn_{12}$ , and  $Fe_8Br_8$  magnetic cluster.

In order to estimate the position of C 2p, N 2p and O 2p-states and their mixing with 3d-states in  $Mn_{12}$  and  $Fe_8Br_8$ , the XES of constituents are converted to the binding energy scale in Figs. 3 and 4 by subtracting the emission energies from the XPS core level binding energies. This comparison of the emission of the constituents with XPS VB (on the binding energy scale) allows estimating the contribution of different states to the formation of the valence band of magnetic clusters  $Mn_{12}$  and  $Fe_8Br_8$ . Based on this compar-

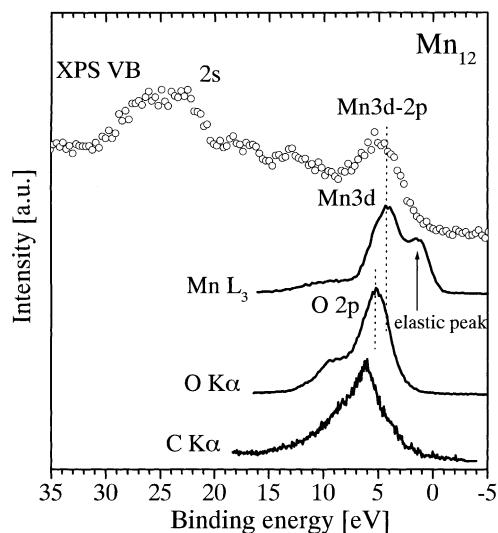


Fig. 3. Comparison of XES of constituents and XPS VB of  $Mn_{12}$  on the common binding energy scale. Mn  $L_3$  XES is resonantly excited at  $L_3$ -threshold; carbon and oxygen  $K\alpha$  XES are excited far from the thresholds at  $E_{exc} = 300$  eV, respectively.

ison, we conclude that 3d-states mainly mix with C 2p, N 2p and O 2p-states and the overlap gives a rather broad XPS p–d peak located at around 6 eV. Non-metallic O 2s-states form quasi-atomic bands located around 15–25 eV.

The electronic structure calculations are shown in Figs. 5 and 6. Values of the magnetic moment for similar but non-equivalent 3d-ions of three different classes are very close (Table 1). The main distinction of the LDA +  $U$  results as compared with the LDA is the non-zero energy gap instead of the finite density of states (DOS) at the Fermi level. For the LDA calculations, the spectral density is strongly

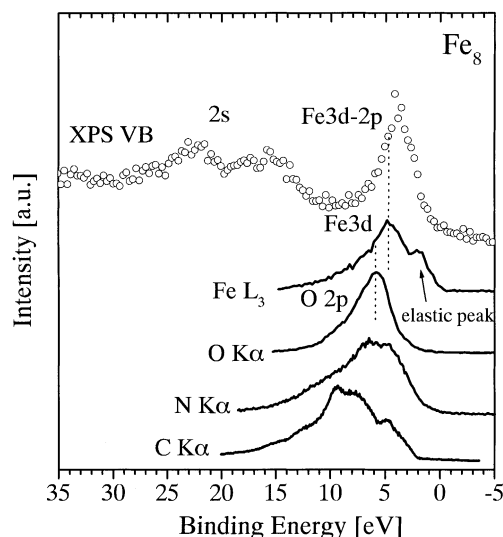


Fig. 4. Comparison of XES of constituents and XPS VB of  $Fe_8Br_8$  on the common binding energy scale. Fe  $L_3$  XES is resonantly excited at  $L_3$ -threshold; carbon, nitrogen and oxygen  $K\alpha$  XES are excited far from the thresholds at  $E_{exc} = 300, 410$  and 560 eV, respectively.

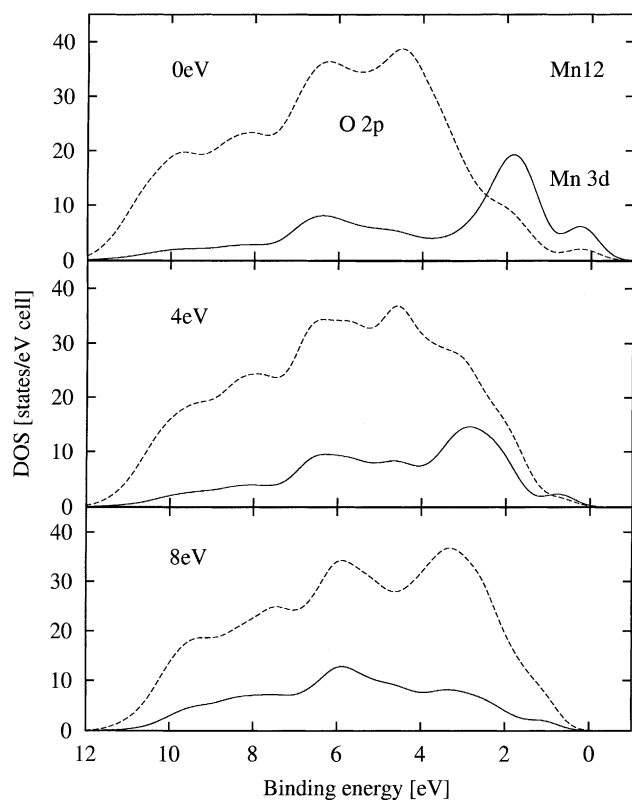


Fig. 5. Mn 3d (solid line) and O 2p (dotted line) DOS of  $\text{Mn}_{12}$  cluster calculated for  $U = 0, 4$  and  $8$  eV. Energy is given in binding energy scale with respect to the Fermi level.

concentrated within a region of  $\pm 2$  eV near the Fermi level, while for the LDA +  $U$  calculations, the DOS is spread uniformly over a range of about 10 eV. The values of band gap, local magnetic moments on 3d-ions and O 2p–3d mixing are found to be very sensitive to the value of parameter  $U$ .

Table 1

Calculated local magnetic moments ( $\mu_B$ ) and band gap (eV) for  $\text{Mn}_{12}$  and  $\text{Fe}_8\text{Br}_8$  magnetic clusters

Cluster	Sites	$U = 0$ eV	4 eV	8 eV
$\text{Mn}_{12}$	$\text{Mn}_1$	−2.41	−2.72	−2.92
	$\text{Mn}_2$	3.51	3.44	3.52
	$\text{Mn}_3$	3.55	3.65	3.84
	Gap	None	1.35	2.01
$\text{Fe}_8\text{Br}_8$	Fe1	4.02	4.80	4.98
	Fe2	4.20	4.86	4.99
	Fe3	−3.56	−4.48	−4.90
	Fe4	−3.42	−4.42	−4.87
	Fe5	3.49	4.17	4.76
	Fe6	3.49	4.24	4.78
	Fe7	3.48	4.23	4.75
	Fe8	3.42	4.22	4.70
	Gap	None	0.85	1.24

We have varied  $U$  parameters from 0 to 8 eV. The best agreement with our experimental spectra is obtained for  $U = 4$  eV, which also gives reasonable values for band gap and magnetic moments of the metal ions.

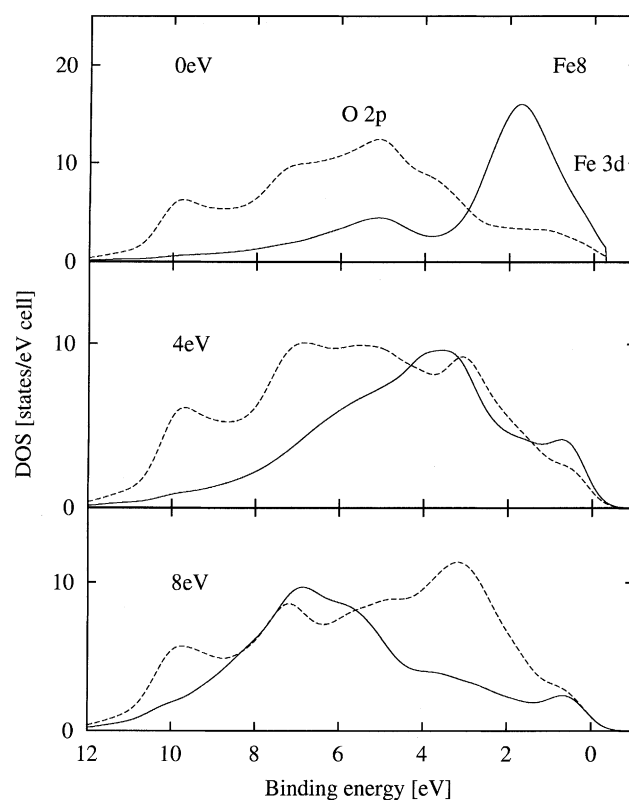


Fig. 6. Fe 3d (solid line) and O 2p (dotted line) DOS of  $\text{Fe}_8\text{Br}_8$  cluster calculated for  $U = 0, 4$  and  $8$  eV. Energy is given in binding energy scale with respect to the Fermi level.

The best agreement with the experimental data is found for  $U = 4$  eV. In this case, we find also reasonable values of the local magnetic moments (see Table 1) and band gaps close to the ones experimentally observed [8]. The positions of 3d and O 2p–3d bands calculated for  $U = 4$  eV (Figs. 4 and 5) are also found in better agreement with experimental spectra (Figs. 2 and 3) than those calculated for other values of  $U$ . The similar results have been obtained for the magnetic cluster  $\text{V}_{15}$  [9].

#### 4. Conclusions

To conclude, we have performed a study of the electronic structure of  $\text{Mn}_{12}$  and  $\text{Fe}_8\text{Br}_8$  magnetic clusters using RIXS and XPS measurements and compared these with our spin-polarized LDA +  $U$  band structure calculations. The on-site repulsion results in a finite energy gap and molecule's magnetic moment being in a good agreement with experimental results. We find that O 2p–3d mixing is very sensitive to the value of  $U$  and the best agreement with the experiment is obtained for  $U = 4$  eV.

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## References

- [1] D. Gatteschi, A. Ganeschi, L. Pardi, R. Sessoli, *Science* 265 (1994) 1054.
- [2] L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* 383 (1996) 145.
- [3] I.V. Solov'yev, K. Terakura, *Phys. Rev. B* 58 (1998) 15496.
- [4] V.I. Anisimov, F. Aryasetiawan, A.I. Lichtenstein, *J. Phys.: Condens. Matter* 9 (1997) 767.
- [5] V.R. Galakhov, A.I. Poteryaev, E.Z. Kurmaev, V.I. Anisimov, S. Bartkowski, M. Neumann, Z.W. Lu, B.M. Klein, T.R. Zhao, *Phys. Rev. B* 56 (1997) 4584.
- [6] D.W. Boukhvalov, A.I. Lichtenstein, V.V. Dobrovitski, M.I. Katsnelson, B.N. Harmon, V.V. Mazurenko, V.I. Anisimov, *Phys. Rev. B* 65 (2002) 184435.
- [7] M.V. Yablonskikh, Yu.M. Yarmoshenko, E.G. Gerasimov, V.S. Gaviko, S. Bartkowski, E.Z. Kurmaev, M. Neumann, *J. Mag. Mater.* 256 (2003) 396.
- [8] Y. Pontillon, A. Ganeschi, D. Gatteschi, R. Sessoli, E. Ressouche, J. Schweitzer, E. Levriev-Berna, *J. Am. Chem. Soc.* 121 (1999) 5342.
- [9] D.W. Boukhvalov, E.Z. Kurmaev, A. Moewes, D.A. Zatspin, V.M. Cherkashenko, S.N. Nemnonov, L.D. Finkelstein, Yu.M. Yarmoshenko, M. Neumann, V.V. Dobrovitskii, M.I. Katsnelson, A.I. Lichtenstein, B.N. Harmon, P. Kogeler, *Phys. Rev. B* 67 (2003) 134408.
- [10] S. Plogmann, Yu.M. Yarmoshenko, T. Schlatholter, M.V. Yablonskikh, E.I. Shreder, A. Wrona, A. Slebarski, E.Z. Kurmaev, J. Braun, M. Neumann, *Phys. Rev. B* 60 (1999) 6428.
- [11] M.V. Yablonskikh, V.I. Grebennikov, Yu.M. Yarmoshenko, E.Z. Kurmaev, S.M. Butorin, L.-C. Duda, J. Nordgren, S. Plogmann, M. Neumann, *Phys. Rev. B* 63 (2001) 235117.
- [12] E.Z. Kurmaev, A. Moewes, S.M. Butorin, M.I. Katsnelson, L.D. Finkelstein, J. Nordgren, P.M. Tedrow, *Phys. Rev. B* 67 (2003) 155105.
- [13] V.I. Grebennikov, V.R. Galakhov, L.D. Finkelstein, N.A. Ovechkina, É.Z. Kurmaev, *Phys. Solid State* 45 (2003) 1048.