Electronic structure of molecular superconductors containing paramagnetic 3d ions

E. Z. Kurmaev and V. R. Galakhov

Institute of Metal Physics, Russian Academy of Sciences—Ural Division, 620219 Yekaterinburg GSP-170, Russia

A. Moewes

CAMD, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806

S. Shimada and K. Endo

Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192 Japan

S. S. Turner and P. Day

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, W1X 4BS, United Kingdom

R. N. Lyubovskaya

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, MD 142432, Russia

D. L. Ederer

Department of Physics, Tulane University, New Orleans, Louisiana 70118

M. Iwami

Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan

(Received 6 March 2000)

The results of x-ray fluorescence measurements of the molecular superconductors $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($T_c = 8.5$ K) and $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($T_c \sim 6$ K) and molecular conductor $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_5\text{H}_5\text{N}$ containing paramagnetic 3d ions are presented. The following transition of the x-ray emission valence spectra are monitored: C $K\alpha$, N $K\alpha$ ($2p \rightarrow 1s$ transition) and Fe $L_{2,3}$, Cr $L_{2,3}$ ($3d4s \rightarrow 2p_{3/2,1/2}$ transition). It is found that the electronic structure of the solvents (benzonitrile, pyridine) that occupy the hexagonal cavities formed by the anionic layer is close to that of the neutral molecule. The ratio of the emission intensities of the peaks L_2 to L_3 for Fe and Cr is found to be 2.8–3.1 times higher for $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ than for pure metals. This indicates that the paramagnetic 3d ions are situated in highly insulating anionic layers. We did not find any changes in the C $K\alpha$ emission for different solvent molecules.

The charge transfer salts based on the donor ET molecule [bis (ethylenedithio) tetrathiafulvalene] cover a wide range of electrical conductivity from highly conducting metallic and superconducting to wide band gap semiconducting and insulating.¹ Typically the crystal structure of such compounds is characterized by the spatial segregation of the organic cations and inorganic anions into alternating layers which can be considered as chemically constructed multilayers.

Among the many ET-based charge transfer salts, new molecular conductors, and superconductors containing paramagnetic Fe^{III} and Cr^{III} ions have been synthesized, such as, $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($T_c = 8.5$ K) (Ref. 2), $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($T_c \sim 6$ K) (Ref. 3), and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_5\text{H}_5\text{N}$ (Ref. 4). In these materials the first superconducting phases containing stoichiometric concentrations of paramagnetic 3d ions were reported.

The crystal structure of these compounds consists of ET layers with +0.5 formal charge per molecule and layers containing H_3O^+ and $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$ ($\text{M} = \text{Cr}, \text{Fe}$). The solvent molecules occupy hexagonal cavities formed by the anionic layer. A most intriguing feature is the change of

the solvent molecule $\text{C}_6\text{H}_5\text{CN}$ (benzonitrile) to $\text{C}_5\text{H}_5\text{N}$ (pyridine) which induces a dramatic change in the observed physical properties: $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ shows a metal-superconductor transition at 8.5 K whereas $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_5\text{H}_5\text{N}$ exhibits a metal-insulator transition at 116 K.^{2,4} Clearly, it is therefore of great interest to examine the electronic structure of these compounds more closely. We present the results of x-ray fluorescence measurements of $(\text{ET})_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($\text{M} = \text{Cr}, \text{Fe}$) and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_5\text{H}_5\text{N}$. Earlier, we applied this method to study the electronic structure of other organic superconductors, namely, $(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ and $(\text{ET})_2\text{Cu}(\text{NCS})_2$ (Ref. 5) and SN_x .⁶ Specifically, the C $K\alpha$, N $K\alpha$ ($2p \rightarrow 1s$ transition) and M $L_{2,3}$ ($3d4s \rightarrow 2p_{3/2,1/2}$ transition) (with $\text{M} = \text{Fe}, \text{Cr}$) x-ray emission spectra probe the occupied C $2p$, N $2p$, Cr $3d4s$, and Fe $3d4s$ density of states that are lying within or close to the valence band.

Single crystals of $(\text{ET})_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ($\text{M} = \text{Cr}, \text{Fe}$) and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_5\text{H}_5\text{N}$ were grown by electrocrystallization in H-shaped cells as previously reported.^{2–4} The single crystals of $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$ were synthesized by electrochemical oxidation of ET under constant

FIG. 1. N $K\alpha$ the emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{CN}$ compared with the experimental N $K\alpha$ emission spectrum of polypyridine (Ref. 10) and the calculated spectrum of the pyridine molecule.

current of 0.5 μA at 40 $^\circ\text{C}$ from solution containing 2×10^{-3} M BEDT-TTF, 1.5×10^{-2} M $\text{Bu}_4\text{NHgBr}_3$ and 10^{-3} trichloroethane and 10^{-3} M HgBr_2 .⁷

The carbon and nitrogen $K\alpha$ ($2p \rightarrow 1s$ transition) and M $L_{2,3}$ ($3d4s \rightarrow 2p_{3/2,1/2}$ transition) ($M = \text{Cr}, \text{Fe}$) spectra were recorded at the Advanced Light Source (Beamline 8.0) employing the University of Tennessee at Knoxville's soft x-ray fluorescence endstation.⁸ Photons with an energy of 300 eV, which is well above the carbon K edge, with an energy of 420 eV (well above the nitrogen K edge), with an energy of 620 eV (well above the chromium L edge) and with an energy of 740 eV, which is well above the iron L edge were delivered to the endstation via the spherical grating monochromator. The carbon and nitrogen $K\alpha$ spectra were obtained with a 600 lines/mm, 10 m radius grating and energy resolution of 0.3–0.4 eV. Cr $L_{2,3}$ and Fe $L_{2,3}$ XES ($3d4s \rightarrow 2p_{3/2,1/2}$) were measured with the second order of the diffraction grating at $E_{\text{exc}} = 620$ and 740 eV, respectively, with an energy resolution of about 0.8 eV. The diffraction grating with 600 lines/mm and $R = 10$ m was used for these measurements. The spectra were calibrated using reference samples of highly oriented pyrographite, hexagonal boron nitride, and Cr and Fe metals. All XES spectra presented in this paper were measured at a temperature of $T = 70$ K to decrease decomposition of the organic compounds during the exposure.

Nonresonant x-ray fluorescence can be described using a two-step model with the emission decoupled from the excitation. The first step corresponds to an electron excitation from a core level to unoccupied states in the conduction band when the sample absorbs an incoming photon. The second step is the emission of the outgoing photon when an electron

FIG. 2. The Fe $L_{2,3}$ emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, Fe_2O_3 , FeO , and Fe metal.

undergoes a transition from the valence band to refill the core level hole created during photon absorption. Both steps are governed by the electric dipole selection rule, $\Delta l = \pm 1$, which means that the $1s$ core level holes in carbon and nitrogen can only be filled by $2p$ valence electrons. For L emission of $3d$ metals, the $2p$ core level holes are filled by $3d$ and $4s$ valence electrons. Therefore x-ray emission spectra (XES) probe partial density of states at each particular atomic site, i.e., XES is site-selective and symmetry restricted.

According to the stoichiometry of the compounds under investigation nitrogen atoms are present only in the solvent molecules which means that by measuring N $K\alpha$ XES we can selectively investigate the electronic structure of included solvents. Figure 1 shows the N $K\alpha$ x-ray emission spectra (XES) of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$. The N $K\alpha$ XES of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$ is compared with that of poly(pyridine-2,5-diyl) (Ref. 10) and the calculated N $K\alpha$ XES spectrum of the neutral pyridine molecule. For the simulation we used a semi empirical MO method called hydrogenic atoms in molecules, version 3 (HAM/3)⁹. Calculations of the valence XES spectra were based on an experimental description of the electronic structure of the pyridine molecule, since the spectral lines correspond to the differences between the total energies of the various excited final states Φ_f , and the initial state Φ_i . The intensity of the line is given by

$$\tau_{if} \propto \left| \int \Phi_i \mathbf{P} \Phi_f d\tau \right|^2, \quad (1)$$

where $\mathbf{P}$ is the associated transition operator. The calculated values for the emission energies were obtained from the differences between binding energies of the core level in which

FIG. 3. The Cr $L_{2,3}$ emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, LiCrO_2 , and Cr metal.

the hole is created and the vertical ionization potentials (VIP's) of the electrons that refill the core hole.

As displayed in Fig. 1 the fine structure of the experimental spectrum of the solvent (pyridine) is in good agreement with the spectrum of polypyridine and also is reproduced quite well by the calculated spectrum of the neutral molecule, which indicates that the electronic structure of solvents which occupy the hexagonal cavities in this class of molecular conductors and superconductors is the same as in the neutral molecules. Therefore, the effect of included solvent molecules on the physical properties of these charge transfer salts is not connected with interactions of solvents with oxalates within the anionic layer.

Figure 2 shows the Fe $L_{2,3}$ x-ray emission spectrum of the oxalate anionic layer of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$. For comparison, the Fe $L_{2,3}$ x-ray emission spectra of Fe metal, FeO, and Fe_2O_3 are also shown. It is known, that the ratio of intensities at the L_2 ($3d4s \rightarrow p_{1/2}$ transition) threshold to L_3 ($3d4s \rightarrow 2p_{3/2}$ transition) threshold differs from the value of $\frac{1}{2}$ as expected from the occupancy of L_2 and L_3 levels and depends on the chemical state of elements.¹¹ For the spectra of 3d metals and alloys, the ratio $I(L_2)/I(L_3)$ is very small due to the Coster-Kronig process $L_2L_3M_{4,5}$.¹² The probability of nonradiative $L_2L_3M_{4,5}$ Coster-Kronig transitions is distinctly lower for 3d oxides than for metals due to the presence of an energy gap. The $I(L_2)/I(L_3)$ intensity ratio should increase on going from pure metals to metal oxides.¹³ Moreover, the $I(L_2)/I(L_3)$ ratio decreases in the sequence $\text{MnO}-\text{Mn}_2\text{O}_3-\text{MnO}_2$.¹⁴ For MnO , with the maximum number of unpaired 3d electrons, the intensity of the Mn L_2 line is nearly equal to that of the Mn L_3 line, but increasing covalency leads to reduction of this ratio. There-

FIG. 4. The C $K\alpha$ emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$ and the reference samples $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$ and polyimide.

fore, the $I(M_L2)/I(M_L3)$ ratio is related to the localization of the 3d electron density and hence the magnetic moment because the exchange interaction energy of the 3d electrons exceeds the spin-orbit interaction energy at least by one order of magnitude which favors a substantial decrease in the statistical weight of the $3d \rightarrow 2p_{3/2}$ transition.

In Fig. 3, the Cr $L_{2,3}$ x-ray emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, the Cr metal and LiCrO_2 are shown. In LiCrO_2 , Cr ions have the electronic configuration $3d^3$.^{14,15} The Cr $L_{2,3}$ spectrum of $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ shows a shoulder at 570 eV, similar to that seen in the sample of LiCrO_2 , which corresponds to the hybridization between Cr 3d and O 2p states.

According to Figs. 2 and 3, the intensity ratio $I(M_L2)/I(M_L3)$ for the samples $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ is almost three times higher than in the pure metals (Fe and Cr) and two times higher than in Fe_2O_3 and LiCrO_2 , respectively. We attribute such large enhancement of this ratio to the highly ionic and insulating character of the oxalate layers and to the localization of the 3d electron density because the local magnetic moments at 3d metal sites are found to be very high: 5.92 and $3.96\mu_B$ for $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, respectively.

Figure 4 shows C $K\alpha$ x-ray emission spectra of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$. The spectra of all compounds exhibit a low-energy sub-band (features 1 and 2) lo-

cated at around 258–263 eV and a main band (features 3 and 4) at $E=268\text{--}284\text{ eV}$. A comparison of these spectra with those of the reference samples $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$ and polyimide shows that the low-energy sub-bands is absent in the spectrum of $(\text{ET})_4\text{Hg}_{2.89}\text{Br}_8$. On the other hand, these sub-bands are present in the C $K\alpha$ XES of polyimide. According to our previous XES studies and MO LCAO calculations of polyimide,¹⁶ these sub-bands arise from the hybridization of C $2p$ states with N $2s$ and O $2s$ states due to the fact that in the chemical structure of polyimide the phenyl rings are linked by nitrogen and oxygen atoms. Therefore we conclude that the low-energy sub-bands in the C $K\alpha$ XES in ET-based charge transfer salts containing oxalates and solvent molecules in the anionic layer arises from the C-N bonds of benzonitrile and pyridine and C-O bonds of oxalates.

The content of carbon atoms in the cationic layer ($\text{C}_{40}\text{H}_{32}\text{S}_{32}$) is three times higher than in the inorganic oxalate layer ($\text{FeC}_6\text{O}_{12}$) together with the solvent molecules ($\text{C}_7\text{H}_5\text{N}$ and $\text{C}_5\text{H}_5\text{N}$). Therefore, the main band of the carbon $K\alpha$ XES will characterize mainly the distribution of C $2p$ states in the ET-conducting layer. The main bands in the C $K\alpha$ XES of $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, $(\text{ET})_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$, and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$ are practically identical and close to the C $K\alpha$ XES of $(\text{ET})_4\text{Hg}_{2.89}\text{I}_8$. In other words there are no changes in the spectra that could be attributed to the replacement of solvent molecules. On the other hand, according to analysis of the crystal structures of

$(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_5\text{H}_5\text{N}$ and $(\text{ET})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{CN}$ given in Ref. 4, changing the solvent molecule from benzonitrile to pyridine induces a disorder in $\frac{1}{4}$ of terminal ethylene groups in the ET layer. Most probably, the energy resolution of C $K\alpha$ XES is not sufficient to reveal this disordering or most likely it is being masked by the 75% of ordered molecules.

In summary we have performed x-ray fluorescence measurements on several new molecular ET-based conductors and superconductors that contain paramagnetic $3d$ ions (Fe and Cr). It is shown that the electronic structure of the solvent molecules (pyridine), which occupy the hexagonal cavities formed by the oxalate anionic layer, is the same as the one found for the corresponding neutral molecules. Furthermore the intensity ratio of $I(\text{ML}_2)/I(\text{ML}_3)$ ($M=\text{Fe}, \text{Cr}$) is three times higher for the molecular superconductors than it is found for pure metals which means that the paramagnetic $3d$ -ions in this class of ET-based charge transfer salts are situated in highly insulating anionic layers. These results confirm what has been seen from magnetic measurements.

This work was supported by the Russian State Program on Superconductivity, the Russian Foundation for Basic Research (Projects No. 00-15-96575 and 99-03-32503), NSF Grants No. DMR-901 7997 and DMR-9420425, the U.S. DOE EPSCOR and Louisiana Education Quality Special Fund [Grant No. DOE-LEQSF (1993-95-03)], and the U.K. Engineering and Physical Sciences Research Council.

- ¹J. H. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Whang, A. M. Kini, and M. H. Whangbo, *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory* (Prentice Hall, Englewood Cliffs, NJ, 1992).
- ²A. W. Craham, M. Kurmoo, and P. Day, J. Chem. Soc., Chem. Commun. **1995**, 2061.
- ³L. Martin, S. S. Turner, P. Day, F. E. Mabbs, and E. J. L. McInnes, J. Chem. Soc., Chem. Commun. **1997**, 1367.
- ⁴S. S. Turner, P. Day, K. M. A. Malik, M. B. Hursthouse, S. J. Teat, E. J. MacLean, L. Martin, and S. A. French, Inorg. Chem. **38**, 3543 (1999).
- ⁵E. Z. Kurmaev, S. N. Shamin, Y.-N. Xu, W. Y. Ching, A. Moewes, D. L. Ederer, E. B. Yagubskii, and N. D. Kushch, Phys. Rev. B **60**, 13 169 (1999).
- ⁶E. Z. Kurmaev, A. I. Poteryaev, V. I. Anisimov, I. Karla, A. Moewes, B. Schneider, M. Neumann, D. L. Ederer, and R. N. Lyubovskaya, Physica C **321**, 191 (1999).
- ⁷R. N. Lyubovskaya, M. Z. Aldoshina, L. M. Gol'denberg, and E. I. Zhilyaeva, Synth. Met. **41-43**, 2143 (1991).
- ⁸J. J. Jia, T. A. Callcott, J. Yurkas, A. W. Ellis, F. J. Himpsel, M. G. Samant, J. Stöhr, D. L. Ederer, J. A. Carlisle, E. A. Hudson, L. J. Terminello, D. K. Shuh, and R. C. C. Perera, Rev. Sci. Instrum. **66**, 1394 (1995).
- ⁹L. Asbrink, C. Fridh, and E. Lindholm, Chem. Phys. Lett. **52**, 63 (1977); Quantum Chem. Program Exchange (QCPE) **12**, 398 (1980).
- ¹⁰M. Magnuson, L. Yang, J.-H. Guo, C. Sathe, A. Agui, J. Nordgren, Y. Luo, H. Agren, N. Johansson, W. R. Salaneck, L. E. Horsburgh, and A. P. Monkman, Chem. Phys. **237**, 295 (1998).
- ¹¹J. E. Holliday, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic Press, London, 1973), p. 713.
- ¹²H. W. Skinner, T. G. Bullen, and J. Jonston, Philos. Mag. **45**, 1070 (1954).
- ¹³V. R. Galakhov, E. Z. Kurmaev, and V. M. Cherkashenko, Izv. Akad. Nauk, Ser. Fiz. **49**, 1513 (1985).
- ¹⁴V. R. Galakhov and E. Z. Kurmaev, Poverkhnost **10**, 107 (1987).
- ¹⁵V. R. Galakhov, E. Z. Kurmaev, St. Uhlenbrock, M. Neumann, D. G. Kellermann, and V. S. Gorshkov, Solid State Commun. **95**, 347 (1995).
- ¹⁶R. P. Winarski, D. L. Ederer, E. Z. Kurmaev, S. N. Shamin, K. Endo, T. Ida, A. Moewes, G. S. Chang, S. Y. Kim, and C. N. Wang, Thin Solid Films **357**, 106 (1999).