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Magnetic Properties of MeB_{50} (Me = 3*d* Atom) Compounds

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Temperature dependence of the static magnetic susceptibility for higher borides MeB_{50}, where Me = V, Cr, Mn, Fe, Co and Ni, was measured by Faraday method in the temperature range of 78–300 K. The value of effective magnetic moment of 3*d*-ions, resulted from the experiment, is compared with corresponding data of the *ab initio* calculations of the electronic structure and magnetic properties of these compounds based on the density functional theory.

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1. Introduction

As is known, the interstitial doping of the β-boron with *d*-elements changes significantly its electronic properties (e.g. transport, thermoelectric and magnetic ones) depending on the kind and concentration of dopants and the type of occupied sites [1–6]. Such behavior originates presumably from the correlation among dopant atoms, accommodated in the well-defined interstitial sites, which generates a system of electronic states in the band gap of boron. One of the effective tools for identification of these impurity states in the boron-rich *d*-metal borides is the study and appropriate analysis of their magnetic properties.

Available literature data on the magnetism of higher 3*d*-metal borides (B:V [4], B:Mn [6], B:Fe [5], B:Ni [4]) refer to compounds with different B:3*d*-metal ratios that makes it difficult to reveal the evolution along 3*d*-series of the physical properties for borides with a fixed fraction of 3*d*-element. Here we report the results of the experimental and theoretical study of magnetic properties of MeB_{50} borides, where Me = V, Cr, Mn, Fe, Co and Ni.

2. Experimental and theoretical details and results

To prepare the samples, a mixture of crushed metal and amorphous boron in a ratio corresponding to MeB_{50} composition has been compacted in "pills", which then were arc melted on a water-cooled copper hearth under an argon atmosphere. The resulting ingots were annealed in a vacuum furnace at about 1650 °C for 20 hours. The obtained samples are assumed to possess the β-rhombohedral boron crystal structure interstitially doped with 3*d* atoms.

Temperature dependence of the magnetic susceptibility $\chi(T)$ was measured by a Faraday method at $T = 78 - 300$ K in a magnetic field of 5 kOe. For all samples, the $\chi(T)$ data obey a modified Curie-Weiss law, $\chi(T) = \chi_0 + C/(T - \theta)$, where χ_0 is temperature independent contribution, C the Curie constant and θ paramagnetic Curie temperature. The Curie-Weiss law parameters, which describe satisfactorily the experimental data (Fig. 1), are collected in Table.

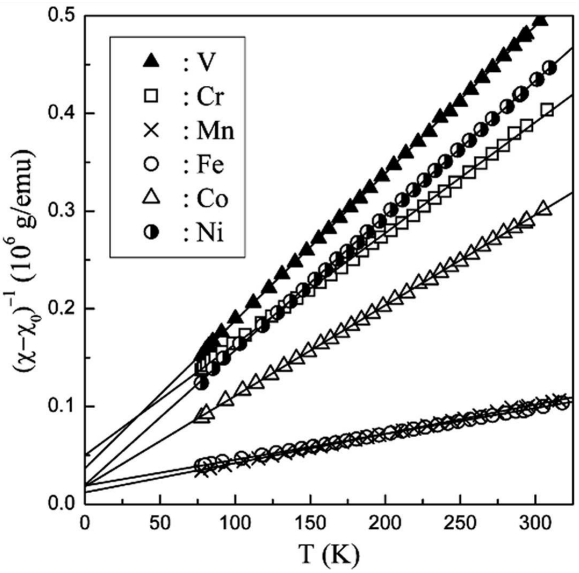

Fig. 1. Temperature dependence of the inverse magnetic susceptibility of MeB_{50} borides (Me = 3*d*-metal).

TABLE

The Curie-Weiss parameters for MeB_{50} compounds, χ_0 (in units of 10^{-6} emu/g), $\theta(K)$ and the resulted from the Curie constant C value of the effective magnetic moment $\mu_{\rm eff}$, together with the calculated ground state moment μ (both in units of $\mu_{\rm B}/3d$ atom).

Me	χ_0	θ	$\mu_{\rm eff}$	μ
V	−0.5	−24	1.77	1.07
Cr	1.5	−42	2.05	2.5
Mn	2.2	−40	4.0	3.3
Fe	1.8	−70	4.26	2.55
Co	0.5	−20	2.27	0.9
Ni	−0.4	−14	1.86	~ 0.1

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The spin polarized calculations of electronic structure and magnetic moment for MeB_{50} borides are carried out by means of FP-LMTO code RSPt [7] for the tetragonal B_{50}-based compounds [8]. The corresponding structure contains four icosahedra of B_{12} whereas two atoms of boron and 3*d*-metal electron donor atom occupy vacant 2*a* positions in the unit cell, providing a stable electronic configuration. Though this structure can be considered as a model one, we should note that B_{12} icosahedra are also essential structural elements of β-rhombohedral boron, which incorporates metal atoms in vacant structural positions [1]. According to FP-LMTO calculations for MeB_{50} compounds in paramagnetic (PM) state, a peculiar evolution of their densities of electronic states $N(E)$ and positions of the Fermi level in the vicinity of the energy gap are substantially dependent on a type of inserted 3*d*-atom of various valency. As is seen in Fig. 2 for FeB_{50} system, the *p*-*d* hybridization and exchange splitting provide the electronic structure and $N(E)$ which are obviously different from that of the elemental semi-conducting boron [8]. The calculations of the spin-polarized electronic structures for ferromagnetic (FM) phase of MeB_{50} borides yield the corresponding magnetic moment values given in Table.

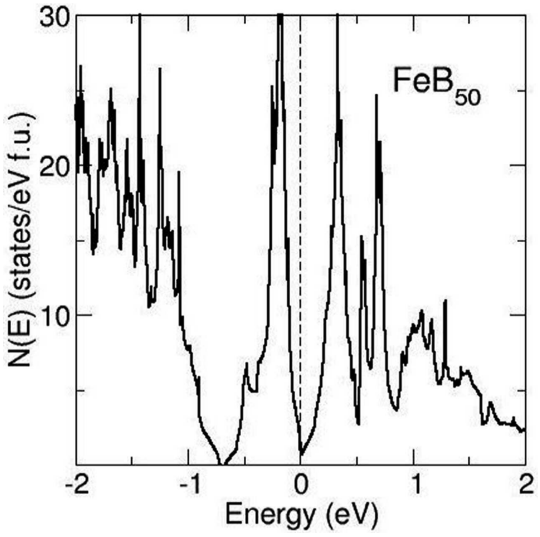

Fig. 2. Density of states for PM FeB_{50}. A strong peak of about 0.6 eV in width just below the Fermi level (dashed line at $E = 0$) originates mainly from the 3*d*-states of Fe.

3. Discussion

As is seen from Table, the experimental values of the effective magnetic moment μ_{eff} show a nonmonotonic behavior reaching its maximum at the middle of the 3*d*-series. The same behavior can be also seen for the calculated moment μ of MeB_{50} compounds for their FM state. This fact clearly indicates the dominating spin nature of the 3*d*-magnetic moment and a substantial quenching of its orbital component in the crystal electric field (CEF).

Another feature of MeB_{50} compounds is the existence of a significant antiferromagnetic (AFM) interaction (see Table) despite a strong dilution of the 3*d*-moments. The largest magnitude of θ (-70 K) was observed for FeB_{50} compound which agrees with data reported in [5] for B:Fe system at the corresponding composition. The nature of this AFM coupling, which is also observed in rare earth higher borides [9], is not yet understood.

The nonmonotonic behavior of the Curie-Weiss parameter χ_0 along 3*d*-series should be also noted. The parameter χ_0 is close to the diamagnetic susceptibility of pure boron ($\sim -0.6 \times 10^{-6}$ emu/g) for VB_{50} and NiB_{50}, having a maximum paramagnetic value of about 2.2×10^{-6} emu/g for MnB_{50} (see Table). Such unusual behavior of χ_0 is assumed to be an intrinsic feature of MeB_{50} systems.

4. Conclusions

The present preliminary results of the experimental and theoretical studies of magnetic properties of MeB_{50} borides (Me = 3*d*-metal) point clearly to the spin nature of the 3*d*-states magnetic moment and almost complete quenching of its orbital part. The most puzzling feature of these borides is the observed existence of AFM coupling. To clarify its origin and a possible role of the CEF effects, we have to carry on the low temperature studies of magnetic properties of MeB_{50} compounds, which are now in progress.

References

[1] H. Werheit, R. Schmechel, V. Kueffell, T. Lundström, *J. All. Comp.* **262-263**, 372 (1997).

[2] H. Werheit, *Solid State Sci.* **13**, 1786 (2011).

[3] U. Kuhlmann, H. Werheit, J. Pelloth, W. Keune, T. Lundström, *Phys. Stat. Sol. B* **187**, 43 (1995).

[4] H. Matsuda, N. Tanaka, T. Nakayama, K. Kimura, Y. Murakami, H. Suematsu, M. Kobayashi, I. Higashi, *J. Phys. Chem. Solids* **57**, 1167 (1996).

[5] G.P. Tsiskarisvili, T. Lundström, L. Lundgren, G.V. Tsagareishvili, D.N. Tsikaridze, F.N. Tavadze, *J. Less-Common Metals* **142**, 91 (1988).

[6] G.P. Tsiskarishvili, T. Lundström, L. Lundgren, G.V. Tsagareishvili, D.N. Tsikaridze, F.N. Tavadze, *J. Less-Common Metals* **147**, 41 (1989).

[7] J.M. Wills, M. Alouani, P. Andersson, A. Delin, O. Eriksson, O. Grechnyev, *Full-Potential Electronic Structure Method*, Springer Verlag, Berlin (2010).

[8] W. Hayami, S. Otani, *J. Solid State Chem.* **183**, 1521 (2010).

[9] T. Mori, *J. Phys.: Conf. Ser.* **176**, 012036 (2009).