Magnetic Properties of MeB\textsubscript{50} (Me = 3\textit{d} Atom) Compounds

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Temperature dependence of the static magnetic susceptibility for higher borides MeB\textsubscript{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\textit{d}-ions, resulted from the experiment, is compared with corresponding data of the \textit{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 \(\beta\)-boron with \textit{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 \(\beta\)-metal borides is the study and appropriate analysis of their magnetic properties.

Available literature data on the magnetism of higher 3\textit{d}-metal borides (B:V \[4\], B:Mn \[6\], B:Fe \[5\], B:Ni \[4\]) refer to compounds with different B:3\textit{d}-metal ratios that makes it difficult to reveal the evolution along 3\textit{d}-series of the physical properties for borides with a fixed fraction of 3\textit{d}-element. Here we report the results of the experimental and theoretical study of magnetic properties of MeB\textsubscript{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\textsubscript{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 \(\beta\)-rhombohedral boron crystal structure interstitially doped with 3\textit{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 \(\chi_0\) is temperature independent contribution, \(C\) the Curie constant and \(\theta\) paramagnetic Curie temperature. The Curie-Weiss law parameters, which describe satisfactorily the experimental data (Fig. 1), are collected in Table.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Me & \(\chi_0\) & \(\theta\) & \(\mu_{\text{eff}}\) \\
\hline
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 & \sim 0.1 \\
\hline
\end{tabular}
\caption{Curie-Weiss parameters for MeB\textsubscript{50} compounds.}
\end{table}

Fig. 1. Temperature dependence of the inverse magnetic susceptibility of MeB\textsubscript{50} borides (Me = 3\textit{d}-metal).

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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 3d-metal electron donor atom occupy vacant 2a 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 3d-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 3d-states of Fe.](image)

### 3. Discussion

As is seen from Table, the experimental values of the effective magnetic moment $\mu_{eff}$ show a nonmonotonic behavior reaching its maximum at the middle of the 3d-series. The same behavior can be also seen for the calculated moment $\mu$ of MeB$_{50}$ compounds for their FM state. This fact clearly indicates the dominating spin nature of the 3d-metallic 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 3d-moment. The largest magnitude of $\theta$ (~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 $\chi_0$ along 3d-series should be also noted. The parameter $\chi_0$ 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 $2.2 \times 10^{-6}$ emu/g for MnB$_{50}$ (see Table). Such unusual behavior of $\chi_0$ 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 = 3d-metal) point clearly to the spin nature of the 3d-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