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Anisotropy of the magnetic properties and the electronic structure of transition-metal diborides

A. V. Fedorchenko,[a] G. E. Grechnev, A. S. Panfilov, A. V. Logosha, and I. V. Svechkarev

B. I. Verkin Institute for Low-Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, pr. Lenina 47, Kharkov 61103, Ukraine

V. B. Filippov, A. B. Lyashchenko, and A. V. Evdokimova

I. N. Frantsevich Institute for Materials Science, ul. Krzhizhanovskogo 3, Kiev 03680, Ukraine

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The temperature dependences of the magnetic susceptibility χ and its anisotropy $\Delta\chi=\chi_\parallel-\chi_\perp$ have been measured for hexagonal single crystals of transition-metal diborides MB_2 ($M=Sc,Ti,V,Zr,Hf$) in the temperature interval 4.2–300 K. It is found that the anisotropy $\Delta\chi$ is weakly temperature-dependent, a nonmonotonic function of the filling of the hybridized $p-d$ conduction band, and largest for group-IV transition metals. First-principles calculations of the electronic structure of diborides and the values of the paramagnetic contributions (spin and Van Vleck) to their susceptibility show that the behavior of the magnetic anisotropy is due to the competition between Van Vleck paramagnetism and orbital diamagnetism of the conduction electrons. © *2009 American Institute of Physics*. [doi:10.1063/1.3266916]

I. INTRODUCTION

Most known transition-metal diborides MB_2 are formed by group III-VI transition elements (Sc, Ti, Zr, Hf, V, Nb, and others) and have a layered hexagonal $C32$ structure of the AlB_2. These compounds are of great scientific and applied interest because of their unique physical-chemical properties,[1] such as high melting temperature, heightened hardness, thermal conductivity, and chemical resistance (inertness), and they are characterized by a large diversity of structural, electronic, and magnetic properties.[1–7]

Even though a large number of experimental studies of the physical properties of diborides have been performed in recent years as a result of the discovery of superconductivity in MgB_2 at $T_c\simeq 39$ K, reliable data on the superconductivity and the magnetic and elastic properties of the compounds MB_2 still are sparse and often contradictory (see, for sample, Ref. 5 and the references cited there). In addition, the existing information on the magnetic properties of diborides[1–3] has been obtained primarily for polycrystalline samples and is very ambiguous because of the differences in sample quality and origin. In recent years, technological progress in growing single-crystal samples of diborides has made it possible to investigate their physical properties, including studying the features of the Fermi surface by means of the de Hass-van Alphen effect, in greater detail and more comprehensively.[6]

The results of experimental and theoretical investigations of the magnetic properties of single crystals of the diborides MB_2 ($M=Sc,Ti,V,Cr,Zr,Hf$) and their relation with the electronic structure are presented in the present article. The main objective of this work is the study of the magnetic susceptibility and its anisotropy in this representative series of isostructural ($C32$) diborides, making it possible to analyze the changes of the magnetic properties as a function of the variations of the lattice parameters and the degree of filling of strongly hybridized $p-d$ states of the conduction band.

Detailed experimental investigations of the magnetic susceptibility of the compounds MB_2 are supplemented by first-principles calculations of their electronic structure as well as the magnetic and elastic properties. The calculations are performed using the FP-LMTO computational method within the framework of the density function theory (DFT).

II. EXPERIMENTAL DETAILS AND MEASUREMENT RESULTS

The diboride single crystals were obtained by the method of crucibleless high-frequency zone melting from initial diboride powders prepared by a solid state reduction reaction of the oxides of the corresponding metals (99.95% purity) with boron (99.9% purity) (see Refs. 6 and 8). Recently published observations of the de Hass-van Alphen effect[6] of this series of samples confirm that the samples prepared by this method are of high quality.

The measurements of the magnetic susceptibility χ were performed by the Faraday method in the temperature interval 4.2–300 K for directions of the magnetic field $H\simeq 1$ T along and perpendicular to the six-fold c axis of the hexagonal structure. The typical experimental temperature dependences $\chi(T)$ for the single-crystal diborides studied are presented in Fig. 1 together with similar data for a polycrystalline sample of chromium diboride CrB_2, whose susceptibility, according to existing experimental data for a single crystal of this compound,[9] does not exhibit appreciable anisotropy. The possible systematic error in the measurements is estimated to be no greater than $0.01\cdot 10^{-4}$ cm^3/mole.

As shown in Fig. 1, the susceptibility of TiB_2 (just as that of the group-IV transition-metal diborides ZrB_2 and HfB_2 not presented in the figure) as well as VB_2 is weakly temperature-dependent and is characterized by appreciable

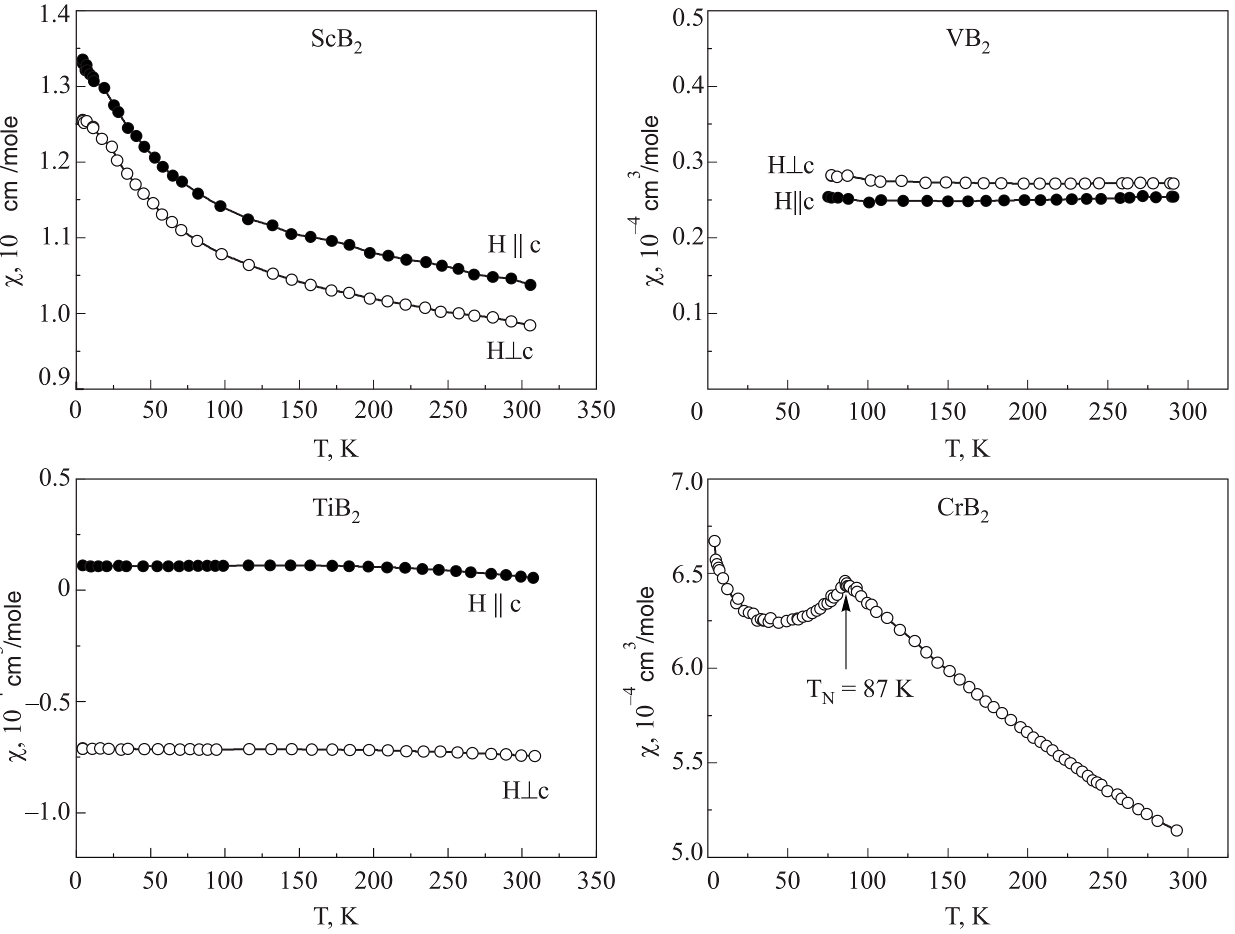

FIG. 1. Temperature dependence of the magnetic susceptibility of certain transition-metal diborides.

anisotropy $\Delta\chi = \chi_\parallel - \chi_\perp$ (the values of the susceptibility $\chi_\parallel$ and $\chi_\perp$ correspond to the directions of the magnetic field along and perpendicular to the axis *c*). A stronger temperature dependence of the susceptibility is observed in ScB$_2$, but the $\Delta\chi$ remains practically constant.

A characteristic of the temperature dependence $\chi(T)$ in CrB$_2$ is a sharp peak at $T_N \simeq 87$ K, corresponding to the transition from a paramagnetic (PM) to an antiferromagnetic (AFM) state with spiral magnetic structure of the helicoidal type,[10] whose magnetic moment (about $0.6\mu_B$ per chromium atom at $T=0$) turns in the *ac* plane. The value found for the transition temperature agrees with the data presented in the literature, $T_N = 85-88$ K.[2,9,10]

The values of the magnetic susceptibility and its anisotropy at room temperature for the diborides studied are presented in Table I, together with the values of the published experimental data from other works. As shown in Table I, the average susceptibility $\bar{\chi}$ and the susceptibility anisotropy $\Delta\chi$ depend strongly and nonmonotonically on the degree of filling of the conduction band of the diborides. The largest anisotropy is observed in group-IV transition-metal diborides, whose distinguishing feature is a pronounced diamagnetic character of the susceptibility. We also note that for some systems, specifically, group-IV metal diborides, there is an appreciable discrepancy between the value of $\bar{\chi}$ for single crystals and the data obtained for polycrystalline samples in early works.[12,13] It can be supposed that the magnetic susceptibility of diborides depends strongly on the sample quality and stoichiometry.

III. COMPUTATIONAL DETAILS AND RESULTS FOR THE ELECTRONIC STRUCTURE

The diborides studied in the present work possess a hexagonal crystalline structure of the type *C*32 with the ratio *c*/*a*

TABLE I. Experimental magnetic susceptibility of MB$_2$ at $T=293$ K.

	$\chi_\parallel$	$\chi_\perp$	$\chi_\parallel - \chi_\perp$	$\bar{\chi} = (\chi_\parallel + 2\chi_\perp)/3$		
MB$_2$	10^{-4} cm^3/mole					
ScB$_2$	1.045	0.989	0.056	1.008;		~0.8[a]
TiB$_2^*$	0.066	−0.740	0.806	−0.471;	−0.40;[b]	0.313[c]
TiB$_2$	0.060	−0.702	0.762	−0.448		
ZrB$_2$	0.094	−0.671	0.765	−0.416		−0.677[c]
HfB$_2$	−0.303	−0.936	0.633	−0.725;		−0.04[c]
VB$_2$	0.255	0.271	−0.016	0.265;	0.215;[b]	0.341[c]
CrB$_2$	—	—	~0[d]	5.14;	5.4;[d]	3.9[c]
NbB$_2$	—	—	—	—		0.08[c]
TaB$_2$	—	—	—	—		−0.648[c]

Note: *F. A. Sidorenko kindly provided the sample.
[a]data of Ref. 11;
[b]Ref. 12;
[c]Ref. 13;
[d]Ref. 9.

TABLE II. Computed values of the bulk modulus B and the contributions to the magnetic susceptibility of diborides.

MB_2	B, GPa	χ_{ston}	$\bar{\chi}_{spin}$	$\bar{\chi}_{orb}$	$\Delta_{\chi orb}$	χ_{dia}	χ^*_{sum}
		10^{-4} cm^3/mole					
ScB_2	240	0.40	0.57	0.39	0.043	−0.10	0.86
TiB_2	290	0.10	0.15	0.99	0.131	−0.12	1.02
VB_2	270	0.68	0.90	0.83	0.080	−0.11	1.62
CrB_2	230	4.0	7.03	0.60	0.010	−0.10	7.53
YB_2	230	0.39	0.43	0.23	0.025	−0.25	0.41
ZrB_2	280	0.08	0.09	0.50	0.053	−0.23	0.36
NbB_2	260	0.38	0.40	0.56	0.068	−0.22	0.74
MoB_2	250	0.58	0.62	0.55	0.008	−0.20	0.97
HfB_2	310	0.07	0.09	0.41	0.032	−0.36	0.14

Note: $\chi_{sum}=\bar{\chi}_{spin}+\bar{\chi}_{orb}+\chi_{dia}$

of the axes close to 1.[1] This crystalline lattice consists of layers of a transition metal alternating with graphite-like layers of boron which are oriented perpendicular to the [001] axis. The electronic structure of diborides was calculated using a modified FP-LMTO method.[14,15] The exchange-correlation potential was taken into account in the local density approximation[16] (LDA) as well as in the generalized gradient approximation[17] (GGA) of the density functional theory (DFT). In the present calculations the FP-LMTO basis set for MB_2 included $2s$, $2p$, and $3d$ orbitals of boron as well as np, $(n+1)s$, $(n+1)p$, and nd orbitals of the metal M, where n is the principal quantum number for the valence d states of the transition metal.

The calculations of the electronic structure were performed for a series of lattice parameters close to the experimental values. The ratio c/a was fixed and corresponded to the experimental value (from Ref. 1) for each compound MB_2. The equilibrium lattice parameters and the corresponding theoretical values of the bulk modulus B were determined from LDA calculations of the volume dependence of the total energy $E(V)$ using the well-known Murnagan equation of state:[14]

$$E(V)=E_0+\frac{BV_0}{B'}\left(\frac{(V_0/V)^{B'-1}}{B'-1}+\frac{V}{V_0}-\frac{B'}{B'-1}\right), \qquad (1)$$

which is based on the assumption that the pressure derivative B' of the bulk modulus B is constant (here the bulk modulus corresponds to the equilibrium volume: $B=B(V_0)$). The values obtained for B' from Murnagan's equation were used to estimate the bulk moduli corresponding to the experimental volumes of the unit cell; these estimates are presented in Table II.

The high values obtained for the elastic moduli of diborides in Table II agree qualitatively with the calculations performed in Ref. 7 in the DFFT-GGA approximation. The literature contains only sparse and conflicting experimental data on the elastic properties of diborides (see Refs. 1 and 7 and the references cited there). The computational results which have been obtained permit making up for the missing experimental data as well as determining the behavioral trends in the bulk moduli of diborides with AlB_2 structure as a function of the filling of the conduction band. The results of these calculations are also of interest in connection with the recent discovery of high values of the elastic moduli for the so-called "ultra-incompressible" (ultraincompressiblity[19]) diborides WB_2, ReB_2, RuB_2, and OsB_2, whose crystal structure differs from that of AlB_2.[1] The values of the elastic moduli of diborides calculated in the present work and given in Table II as well as the results of recent experimental[19] and theoretical[7] studies show that the previously published computed values[4] of the bulk moduli of hexagonal diborides are strongly understated, probably because the atomic spheres approximation (ASA) was used to calculate the total energy of MB_2.

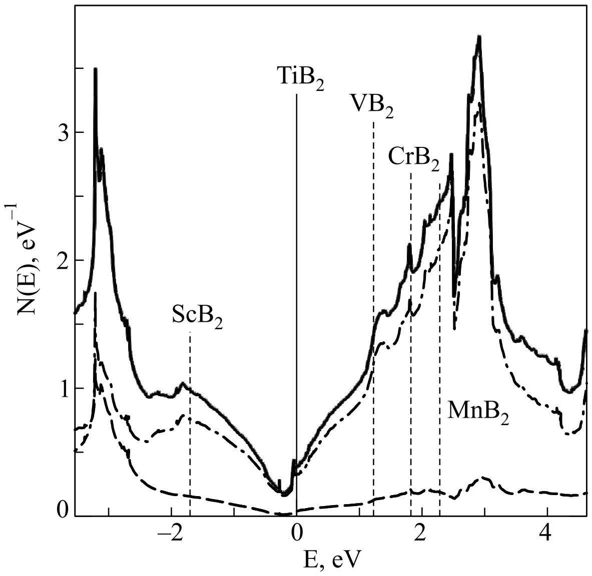

FIG. 2. TiB_2 electron density of states. The total $N(E)$ and partial contributions of the d states of titanium and the p states of boron are marked with solid, dashed, and dot-dash lines, respectively. The vertical lines correspond to the fillings levels of the conduction band for the corresponding 3d-metal diborides.

The computed electron densities of states $N(E)$ of diborides are quite similar but differ in the details and the position of the Fermi level E_F (see Fig. 2). The vertical lines in Fig. 2 correspond to the filling levels of the conduction band for the corresponding $3d$-metal diborides (in the rigid band approximation). According to the present calculations, the partial densities of states in Fig. 2 indicate strong hybridization of the d states of the transition metal with the p states of boron. It can also be expected that the filling of the conduction band and variations of $N(E_F)$ in a number of the diborides will largely determine the physical properties of the compounds MB_2.

For group-IV (TiB_2, ZrB_2, HfB_2) and -V (VB_2, NbB_2, TaB_2) transition-metal diborides, the bonding electronic states are filled while the antibonding stats are practically unoccupied. Such a conduction-band structure explains the hardness and high chemical stability of these borides. The Fermi level in the series ScB_2–MnB_2 (Fig. 2) as well as in YB_2–MoB_2 passes through a deep minimum in $N(E)$, which corresponds to a pseudogap in the electronic energy spectrum, and passes into a region of antibonding states and large values of $N(E_F)$. This results in instability of the $C32$ phase of diborides starting from the center of the $3d$ and $4d$ series of the transition metals.

IV. COMPUTATIONAL DETAILS AND RESULTS FOR THE MAGNETIC PROPERTIES

The FP-LMTO calculations of the field-induced spin and orbital (Van Vleck) magnetic moments were performed for diborides in an external magnetic field $H=10$ T. The effect of the external magnetic field on the electronic structure was taken into account self-consistently on the basis of the local spin-density approximation (LSDA) following Refs. 15 and 18 by including the Zeeman operator in the FP-LMTO Hamiltonian:

$$\mathcal{H}_Z = \mu_B \mathbf{H} \cdot (2\hat{\mathbf{s}} + \hat{\mathbf{l}}). \tag{2}$$

Here $\hat{\mathbf{s}}$ is the spin operator and $\hat{\mathbf{l}}$ is the orbital angular momentum operator. The induced spin and orbital magnetic moments computed in an external field make it possible to obtain the corresponding volume magnetizations, while the relation between the magnetization and intensity of the field contributes to the paramagnetic susceptibility, χ_{spin} and χ_{orb}. For the $C32$ hexagonal crystalline structure the components of these contributions, $\chi_{i\parallel}$ and $\chi_{i\perp}$, were obtained for the external magnetic field directed parallel and perpendicular to the c axis, respectively. The average values of the computed components χ_{spin} and χ_{orb}, $\hat{\chi}=(\chi_{i\parallel}+2\chi_{i\perp})/3$, as well as the anisotropy of the orbital contribution $\Delta\chi_{\mathrm{orb}}=\chi_{\mathrm{orb}\parallel}-\chi_{\mathrm{orb}\perp}$ are presented in Table II.

The exchange-enhanced Pauli spin contribution to the magnetic susceptibility was also calculated, for comparison, in the Stoner model:

$$\chi_{\mathrm{ston}} = S\chi_P \equiv \mu_B^2 N(E_F)[1 - IN(E_F)]^{-1}, \tag{3}$$

where $\chi_P=\mu_B^2 N(E_F)$, S is the Stoner enhancement factor, and μ_B is the Bohr magneton. The Stoner integral I, characterizing the exchange-correlation interaction of the conduction electrons, can be expressed using the computed parameters of the electronic structure (see Ref. 20 and the references cited there):

$$I = \frac{1}{N(E_F)^2} \sum_{qll'} N_{ql}(E_F) J_{qll'} N_{ql'}(E_F). \tag{4}$$

Here $N(E_F)$ is the total electron density of states at the Fermi level E_F, $N_{ql}(E_F)$ are the partial densities of states for atom q in a unit cell, $J_{qll'}$ are the local exchange integrals

$$J_{ll'} = \int g(\rho(r)) \phi_l^2(r) \phi_{l'}^2(r) dr, \tag{5}$$

where $\phi_l(r)$ are the partial wave functions and $g(\rho(r))$ is the charge density function.[16] The values of the exchange-enhanced Pauli susceptibility χ_{ston} calculated in the Stoner approximation are also presented in Table II.

V. DISCUSSION

The calculation of the magnetic susceptibility of a metallic system remains to this day a very difficult problem (see Refs. 15 and 21 and the references cited in these works). The total susceptibility in the absence of a spontaneous magnetic moment can be express in general form as

$$\chi_{\mathrm{tot}} = \chi_{\mathrm{spin}} + \chi_{\mathrm{orb}} + \chi_{\mathrm{dia}} + \chi_L, \tag{6}$$

where the terms are, respectively, the Pauli spin susceptibility (χ_{spin}), the Van Vleck orbital paramagnetism (χ_{orb}), the Langevin diamagnetism of the electron shells of ions (χ_{dia}), and the orbital diamagnetism of the conduction electrons (χ_L).

In this work the computed contributions to χ from Table II were used to analyze the experimental data on the magnetic susceptibility and its anisotropy in diborides. The Langevin diamagnetic contribution for diborides can be estimated using the results of Refs. 21–23 and the values of χ_{dia} fall between the corresponding susceptibilities of free atoms and ions (see Table II). Evidently, the terms χ_{diam} do not contribute to the observed anisotropy $\Delta\chi$.

As shown in Table II, the orbital Van Vleck susceptibility χ_{orb} makes a substantial contribution to the total paramagnetic susceptibility in nonmagnetic transition-metal diborides. In group-V transition-metal diborides χ_{orb} is comparable to χ_{spin}, and in ground-IV metal diborides (TiB_2, ZrB_2, HfB_2) χ_{orb} is much greater than χ_{spin}. Likewise, Table II shows that Stoner's model gives smaller values for the spin susceptibility χ_{ston} as compared to χ_{spin}, calculated in an external magnetic field. This agrees with the results of Ref. 18, according to which taking account of the nonuniform spin density distribution in the unit cell properly in the FP-LMTO-LSDA calculations in an external field substantively improves the agreement of the computed spin susceptibility (χ_{spin}) and the magnetovolume effect in paramagnetic metallic systems with experiment as compared with the Stoner approximation.

The calculation of the diamagnetic contribution χ_L is a much more complicated problem (see Refs. 21 and 24–28 and the references cited in these works). Together with the known Landau-Peierls contribution, χ_L also contains substantial contributions of an interband nature from the occupied states of the electronic spectrum.[24] The well-known Landau contribution for diamagnetism of free electrons χ_L^0 is $-1/3$ times the corresponding Pauli spin susceptibility and is often used for making estimates. However, for many metallic systems this rough approximation does not give even the order of magnitude of the diamagnetic susceptibility of the conduction electrons.[27,29,30]

According to the experimental data in Table I, as well as in Fig. 1, the observed anisotropy turns out to be large and practically temperature-independent for group-IV transition-metal diborides. As Table II shows, the computed anisotropy of the Van Vleck paramagnetic contribution χ_{orb} is only $\sim$10% of the experimental values of $\Delta\chi$ for these diborides. In addition, there is also an appreciable discrepancy between the sum of the computed contributions in the magnetic susceptibility $\chi_\Sigma=\bar{\chi}_{\mathrm{spin}}+\bar{\chi}_{\mathrm{orb}}+\bar{\chi}_{\mathrm{dia}}$ in Table II and the experimental values $\chi_{\mathrm{exp}}=\bar{\chi}$ in Table I. These discrepancies can be attributed to the diamagnetic contribution χ_L in Eq. (6), which for group-IV metal diborides can be estimated as $\chi_L=\chi_{\mathrm{exp}}-\chi_{\mathrm{sum}}\simeq-10^{-4}$ cm^3/mole. The relatively large value of this susceptibility, which is much greater than the diamagnetism in Landau's free-electron approximation χ_L^0, requires explanation.

It has been established previously that even small groups of quasi-degenerate electronic states with small effective

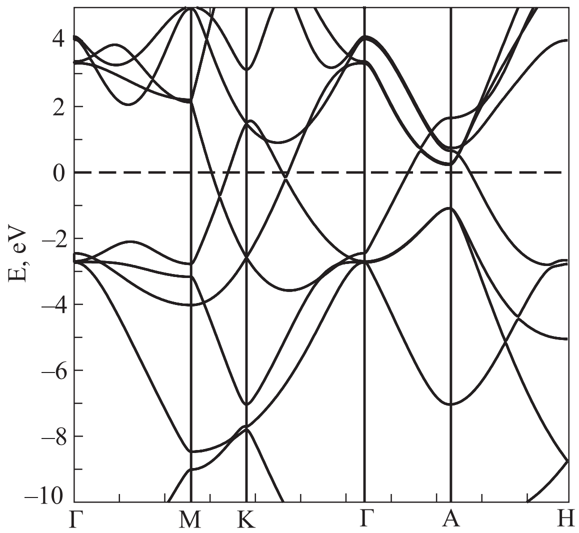

FIG. 3. ZrB_2 band structure along the directions of symmetry of the Brillouin zone. The horizontal dashed line marks the Fermi level.

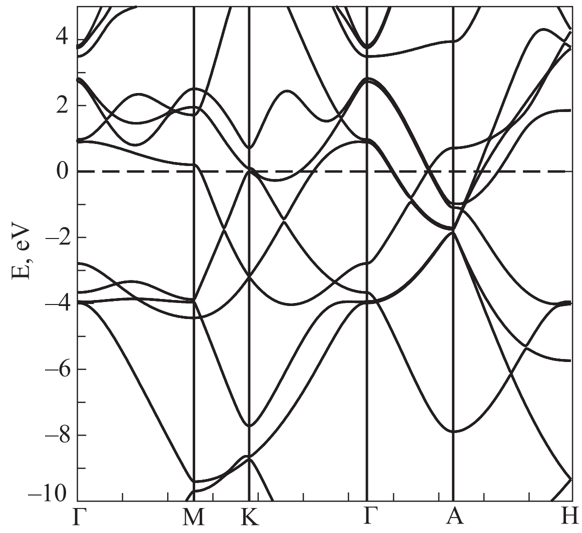

FIG. 4. NbB_2 band structure along the directions of symmetry of the Brillouin zone. The horizontal dashed line marks the Fermi level

masses, located in direct proximity to the Fermi level E_F (about 0.1 eV or closer), make the dominant and anisotropic orbital diamagnetic contributions to the susceptibility of many nontransition metals (graphite,[26] the alloys Cd–Mg and Cd–Hg,[27] Be,[29] Al,[30] Zm,[31] In,[32] the alloys Bi–Sb[33]) and even systems with a large admixture of *d* and *f* states near E_F ($YbPb_3$, $YbSn_3$,[34] and the alloys $La(In,Sn)_3$[35]). In such systems the contributions of χ_L can be many times greater than the Landau estimate χ_L^0 for free-electron diamagnetism, and this anomalous diamagnetism is due to small effective masses of the charge carriers, small spin-orbit splitting in the spectrum, and relative closeness of the critical points of the spectrum to E_F.[24] In this connection it should be noted that within the framework of first-principles DFT calculations the fine details of the spectrum $E(k)$, specifically, the position of the critical points of the spectrum or the points of degeneracy of the energy bands relative to E_F, can be reliably determined to within 0.1 eV.

As shown in Fig. 3, the calculations of the band structure indicate the presence of quasi-degenerate hybridized electronic states close to E_F in the representative diboride of group-IV metals ZrB_2. Similar quasi-degenerate states with small effective masses near E_F are also present in other group-IV metal diborides, TiB_2 and HfB_2, on the KΓ line and near the symmetry point A (see Fig. 3). The intersection of the bands on the line KΓ is especially important in connection with the manifestation of the anomalously strong diamagnetism from states with small effective masses near similar points of degeneracy of the bands.[26,29,33] It should be noted that states with very small cyclotron masses (about 0.1 times the free-electron mass) were observed in recent studies of the de Haas-van Alphen effect in ZrB_2 and HfB_2.[6] The similarity of the band structures of TiB_2, ZrB_2, and HfB_2 as well as the closeness of the values of $\bar{\chi}$ and $\Delta\chi$ (see Table I) for these compounds suggests that the quasi-degenerate states mentioned above can determine the high diamagnetism and susceptibility anisotropy of group-IV transition-metal diborides.

Comparing the experimental data on the susceptibility of group-V transition-metal diborides (VB_2, NbB_2, and TaB_2, see Table I) with the computed contributions χ_{spin}, χ_{orb}, and χ_{dia} from Table II likewise suggests that conduction electrons make a substantial diamagnetic contributions in their susceptibility. Even though VB_2 is a paramagnet it turns out that the diamagnetic contribution χ_L practically compensates the large contributions of χ_{spin} and χ_{orb}. We note that even the sign of $\Delta\chi_{\mathrm{orb}}$ in Table II does not agree with the experimental $\Delta\chi$ for VB_2. This attests that only large anisotropy of χ_L can compete with $\Delta\chi_{\mathrm{orb}}$ and exceed it.

The computed band structure of the diboride NbB_2 is shown in Fig. 4, where quasi-degenerate states with small effective masses can be seen near the Fermi level, specifically, band crossing on the line ΓA as well as states near the symmetry point K. Similar features in the electronic spectrum near E_F also appear in other group-V metal diborides—VB_2 and TaB_2.

It should be underscored that the theoretical calculation of χ_L is a very complicated procedure, which must include a search of groups of quasi-degenerate states of the electronic spectrum near E_F, the construction of a multiband $\mathbf{k}\cdot\mathbf{p}$ model of the spectrum for such states, and then an analytical or numerical calculation of the susceptibility within the framework of a strict theory of the orbital diamagnetism of conduction electrons.[25] The laboriousness of the calculation of orbital susceptibility χ_L is due to, first and foremost, the dimension the matrix $\mathbf{k}\cdot\mathbf{p}$ of the Hamiltonian (see Refs. 26–28). Such calculations of χ_L fall outside the scope of the present work; here, as a first step, the electronic states near E_F, which can be sources of the large diamagnetism and susceptibility anisotropy of the group-IV and -V metal diborides, are determined.

The diborides ScB_2 and CrB_2 investigated in the present work are paramagnets with comparatively small diamagnetic contributions in χ (compare Tables I and II). As one can see from the data in Table II, for both diborides the computed spin susceptibility χ_{spin} is appreciably greater than the corresponding estimate χ_{ston} calculated in the Stoner model. In

ScB_2 the orbital van Vleck contribution χ_{orb} is comparable in magnitude to χ_{spin} and necessary in order to describe the experimental data on the susceptibility. On the whole, the computed anisotropy of χ_{orb} agrees qualitatively with the experimental data on $\Delta\chi$ in ScB_2 and CrB_2 (Table I). For ScB_2 the sum of the computed paramagnetic contributions has turned out to be somewhat less than the experimental susceptibility. It should be noted that the contributions and in an external magnetic field correspond to the ground state of ScB_2 in the LSDA approximation, i.e. to the theoretical values of the lattice parameters, which turn out to be systematically 1–2% less than the experimental values for metallic systems.[14] Thus, the corresponding values of the paramagnetic susceptibility in Table II can be regarded as a lower estimate for χ_{spin} and χ_{orb}, since they correspond to a somewhat "broadened" conduction band in ScB_2.

The Fermi level in the diboride CrB_2 lies on a steep slope of the peak in the density of states, where $N(E)$ increases rapidly with energy and the d states of chromium make the main contribution to $N(E_F)$. Stoner's criterion is practically satisfied, $IN(E_F) \simeq 1$, and the enhancement factor obtained for the spin susceptibility, $S=8$, agrees with the estimates made in Refs. 3 and 4 ($S \simeq 10$). In the paramagnetic phase of CrB_2 the paramagnetic susceptibility increases with decreasing temperature, reaching the value $\chi_{\mathrm{exp}} \simeq 6.5 \cdot 10^{-4}$ cm^3/mole at $T=90$ K. Extrapolation of the susceptibility $\chi_{\mathrm{exp}}(T \to 0)$ from the paramagnetic region (87 K $< T <$ 300 K) gives the estimate $\chi_{\mathrm{exp}}(0) \simeq 7.3 \cdot 10^{-4}$ cm^3/mole, which agrees with the computed paramagnetic contributions χ_{spin} and χ_{orb} from Table II.

VI. CONCLUSIONS

The magnetic susceptibility of the diborides ScB_2, TiB_2, VB_2, ZrB_2, and HfB_2 has been studied for the first time for a single crystal in the temperature range 4.2–300 K. A transition into the superconducting state was not found in any of the diborides studied, right down to liquid-helium temperature. It was established that the value of the susceptibility anisotropy $\Delta\chi$ depends strongly on the filling of the hybridized $p-d$ conduction band and turned out to be large for titanium-group diborides.

First-principles calculations of the electronic structure in an external magnetic field made it possible to determine the values and anistropy of the spin and Van-Vleck orbital paramagnetic contributions to the susceptibility of diborides. It was demonstrated that the LSDA approximation of the density functional theory within the framework of the FP-LMTO method gives an adequate description of the magnetic properties of the compounds ScB_2 and CrB_2.

Comparing the experimental and computed susceptibilities for group-IV and -V transition-metal diborides indicates the presence of a large and anisotropic diamagnetic contribution, which had been neglected, of the order of -10^{-4} cm^3/mole; this contribution can be attributed to a generalized orbital diamagnetism of the conduction electrons χ_L. It is presumed that the large value of χ_L in group-IV and -V metal diborides is due to the presence of quasi-degenerate electronic states with a small effective mass near the Fermi level.

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[a] Email: fedorchenko@ilt.kharkov.ua

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