# Effect of pressure on the magnetic properties of CrB$_2$

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Magnetic susceptibility $\chi$ of the itinerant antiferromagnet CrB$_2$ with $T_N \simeq 87$ K was studied as a function of the hydrostatic pressure up to 2 kbar at fixed temperatures 78 and 300 K. The pressure effect on $\chi$ is found to be negative in sign and weakly dependent on the magnetic state of the compound. In addition, the measured pressure dependence of the Néel temperature, $dT_N/dP = (0.1 \pm 0.1)$ K/kbar, is roughly two orders of magnitude smaller than the corresponding value for the pure chromium. The main contributions to $\chi$ and their volume dependence are calculated *ab initio* within the local spin density approximation, and appeared to be in close agreement with the experimental data.

## 1. Introduction

CrB$_2$ is an itinerant-electron antiferromagnet with the Néel temperature $T_N = 85$–88 K [1–4], possessing a hexagonal crystal structure of AlB$_2$ type. As it follows from the neutron diffraction study on a single crystal, CrB$_2$ has a complicated helicoidal magnetic structure, and the magnetic moment (of about 0.5 $\mu_B$ per Cr atom at $T = 0$) turns in *ac* plane [5]. The electronic specific heat coefficient of CrB$_2$, $\gamma = 13.6$ mJ/(K$^2$·mol) [3], is abnormally high in comparison with those of the nonmagnetic 3$d$-metal diborides such as ScB$_2$, TiB$_2$, VB$_2$ (1–5 mJ/(K$^2$·mol) [2,3,6]). The electronic spin susceptibility of CrB$_2$ is also an order of magnitude higher than that of other diborides, demonstrating a large exchange-enhancement effect. The band structure calculations for CrB$_2$ [7–10] have shown that its Fermi level lies in a region of the high density of electronic states (DOS). Therefore the Stoner criterion is

nearly fulfilled in CrB$_2$, and the susceptibility enhancement factor, $S \simeq 9$, was estimated [7,9]. In addition, the spin density wave (SDW) along the hexagonal axis was predicted in Ref. 7 to be due to the nesting of the 7th-band Fermi surface. However, both the predicted SDW type of magnetic structure and the estimated magnetization of $\sigma \simeq 0.01\mu_B$ per Cr atom are inconsistent with the experimental neutron data [5]. It should be noted that more reasonable value of magnetization, $\sigma \simeq 0.3\,\mu_B$ per Cr atom, was obtained in the recent spin-polarized band structure calculations for CrB$_2$ [10].

Here we report results of our investigations of the pressure effect on the magnetic susceptibility and Néel temperature of CrB$_2$ compound to clarify the nature of its magnetic properties and details of the antiferromagnetic (AFM) transition. The experimental data are supplemented by *ab initio* calculations of the volume dependent band structure and magnetic susceptibility.

## 2. Experimental details and results

The polycrystalline sample of $CrB_2$ compound was initially prepared by arc-melting of the stoichiometric amount of Cr and B elements of better than 99.8% purity in a water cooled crucible under protective argon atmosphere. The ingot was then crushed to powder and pressurized. The pressed sample was sintered at $T \simeq 1500$ °C followed by its melting in an inductance furnace and annealing. The study of x-ray powder diffraction at room temperature revealed that sample has the $AlB_2$-type hexagonal crystal structure, and the obtained lattice parameters agree closely with that published in literature [11]. Any other phases were not detected within the resolution of the employed x-ray technique.

For additional examination of the sample quality, its magnetic susceptibility was measured as a function of temperature for the magnetic field $H = 0.8$ T using the Faraday microbalance method. The data obtained show a clear peak at $T \simeq 87$ K (see Fig. 1), which corresponds to magnetic ordering in the system. The observed $\chi(T)$ behavior is in agreement with the known literature data for the high quality $CrB_2$ samples [4].

The pressure effect on the magnetic susceptibility was measured under helium gas pressure up to 2 kbar at two fixed temperatures, 78 and 300 K, using a pendulum-type magnetometer placed into the nonmagnetic pressure cell [12]. The relative errors of our measurements, performed in the magnetic field $H = 1.7$ T, did not exceed 0.05%. The experimental pressure dependencies of the magnetic susceptibility of $CrB_2$ are shown in Fig. 2, which demonstrate a magnitude of the pressure effect and its linear behavior. For each temperature the values of $\chi$ at ambient pressure and their pressure derivatives $d \ln \chi/dP$ are listed in Table 1. In order to transform the pressure derivative
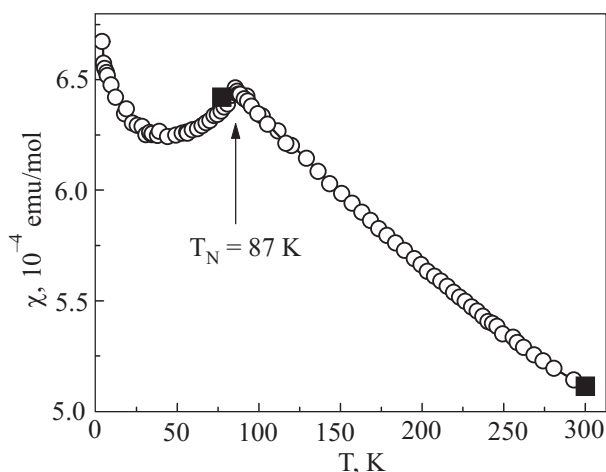


*Fig. 2.* Pressure dependence of the magnetic susceptibility for $CrB_2$ at $T = 78$ and 300 K normalized to its value at $P = 0$.

into the volume one, we used the calculated bulk modulus value ($B = 2.3$ Mbar, see Sec. 3.1).

Table 1. The magnetic susceptibility of $CrB_2$ (in $10^{-4}$ emu/mol) and its pressure (in $Mbar^{-1}$) and volume derivatives at different temperatures

| T, K | $\chi$ | | $d \ln \chi/dP$ | $d \ln \chi/d \ln V$ | |
| --- | --- | --- | --- | --- | --- |
| | exp. | theor.[a] | exp. | exp. | theor.[a] |
| 0 | 7.3[b] | 7.5 | – | – | 4.0 |
| 78 | 6.42 | – | $-1.82 \pm 0.3$ | $-4.2 \pm 0.7$ | – |
| 300 | 5.11 | – | $-1.65 \pm 0.2$ | $-3.8 \pm 0.5$ | – |

[a]for paramagnetic state; [b]extrapolation of the experimental data for paramagnetic state in Fig. 1.

With the aim of finding the pressure effect on the Néel temperature, the $\chi(T)$ dependence was studied in detail around $T_N$ for two different pressures (see Fig. 3). The resulting pressure derivative $dT_N/dP = (0.1 \pm 0.1)$ K/kbar was estimated from a shift of the maximum in $\chi(T)$ and appears to show only weak tendency for an increase of $T_N$ with pressure.

## 3. Computational method and results

### 3.1. Band structure calculations

The investigated diboride $CrB_2$ possesses the hexagonal $AlB_2$ ($C32$) crystal structure which is composed of transition metal layers alternating with graphite-like boron layers stacked perpendicularly to the [001] axis. *Ab initio* calculations of the electronic structure of $CrB_2$ were carried out by employing a modified FP-LMTO method [13–15]. The exchange-correlation potential was treated



*Fig. 1.* Temperature dependence of the magnetic susceptibility for $CrB_2$. The data obtained with pendulum magnetometer at $P = 0$ are presented by filled squares.
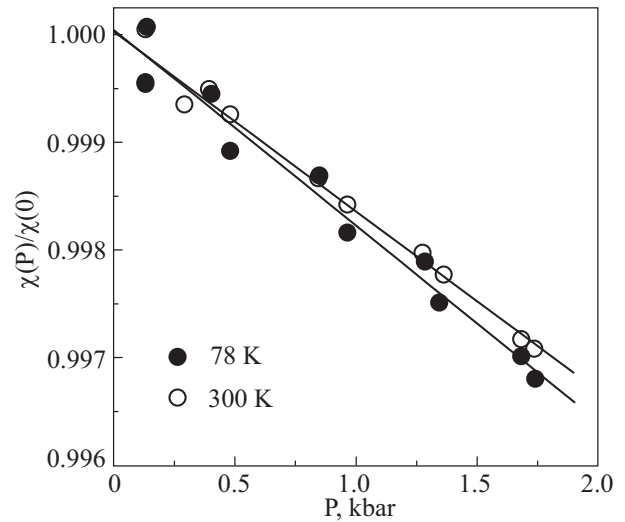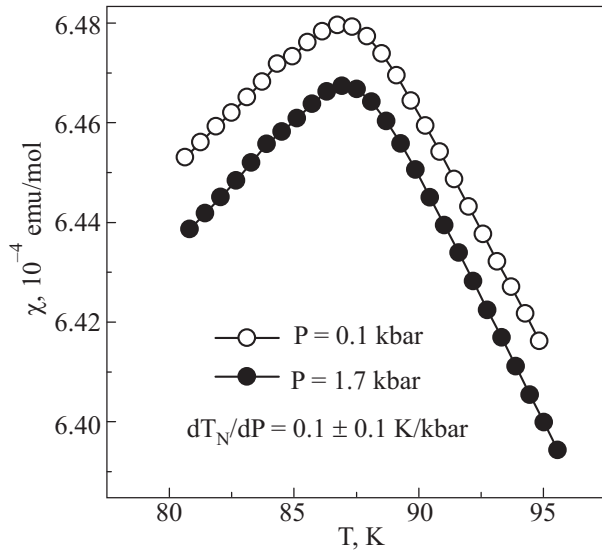
*Fig. 3.* Temperature dependence of the magnetic susceptibility for CrB$_2$ in the vicinity of $T_N$ at two fixed pressures.



*Fig. 4.* Density of states for CrB$_2$. The vertical lines indicate the conduction band filling for the corresponding 3$d$ diborides.

in the local density approximation (LDA) [16] of the density functional theory.

The calculated density of states $N(E)$ for the paramagnetic (PM) phase of CrB$_2$ is shown in Fig. 4, and it is in a qualitative agreement with the results of KKR-ASA [7] and LMTO-ASA [8–10] calculations. The calculated DOS at the Fermi level $N(E_F) = 31.7$ Ry$^{-1}$ is comparable with the results of LMTO-ASA calculations, 33.7 [8] and 34.9 [10] Ry$^{-1}$, but differs substantialy from the earlier result of non-self-consistent calculations of Ref. 7, $N(E_F) = 20.9$ Ry$^{-1}$. As seen from Fig. 4, in CrB$_2$ the Fermi level is located at the steep slope of $N(E)$ peak where DOS rapidly grows with energy. Among other 3$d$-diborides CrB$_2$ possesses a comparatively large value of $N(E_F)$, resulting in a strongly enhanced spin paramagnetism of the compound and transition to the magnetically ordered state at $T = 87$ K.

In order to evaluate the bulk modulus value to be used in the analysis of the pressure effects in CrB$_2$, the band structure calculations were performed for a number of lattice parameters close to the experimental ones (the ratio $c/a$ was fixed at its experimental value 1.033). The equilibrium unit cell volume $V_{th}$ and the corresponding theoretical bulk modulus $B_{LDA}$ were determined from the calculated volume dependence of the total energy $E(V)$ by using the well known Murnaghan equation [14], and appear to be $V_{th} = 21.79$ Å$^3$ and $B_{LDA} = 3.23$ Mbar. The Murnaghan equation is based on the assumption that the pressure derivative $B'$ of the bulk modulus $B$ is constant. By using the evaluated from the Murnaghan equation value of $B' = 3.9$, we have estimated $B \simeq 2.3$ Mbar, corresponding to the *experimental* volume $V_{exp} = 23.41$ Å$^3$ [17]. This correction counterbalances the well known over-bonding tendency of the LDA approach [14], and provides better

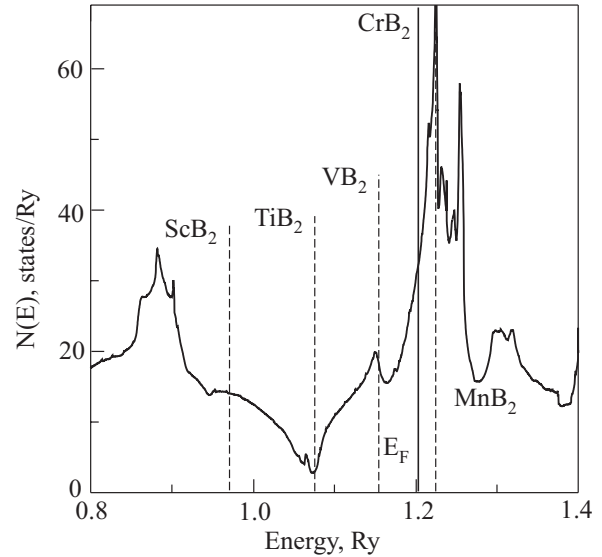agreement with experimental values of bulk moduli, as it comes from our previous calculations [13,15].

### 3.2. Magnetic susceptibility

The FP-LMTO calculations of the field-induced spin and orbital (Van Vleck) magnetic moments were carried out self-consistently within the procedure described in Refs. 13, 15 by means of the Zeeman operator,

$$\hat{H}_Z = \mathbf{H} \cdot (2\hat{\mathbf{s}} + \hat{\mathbf{I}}), \qquad (1)$$

which was incorporated in the original FP-LMTO Hamiltonian. Here $\mathbf{H}$ is the external magnetic field, $\hat{\mathbf{s}}$ and $\hat{\mathbf{I}}$ are the spin and orbital angular momentum operators, respectively. The field induced spin and orbital magnetic moments were calculated in the external field of 10 T and provided estimation of the related contributions to the magnetic susceptibility, $\chi_{spin}$ and $\chi_{orb}$. For the hexagonal $C32$ crystal structure of CrB$_2$, the components of these contributions, $\chi_{i\parallel}$ and $\chi_{i\perp}$, were derived from the magnetic moments obtained in an external field, applied parallel and perpendicular to the $c$ axis, respectively. The averaged values of the calculated $\chi_{spin}$ and $\chi_{orb}$ components, $\chi_i = (\chi_{i\parallel} + 2\chi_{i\perp})/3$, and the evaluated magnetic anisotropy, which is determined by the orbital contribution, $\Delta\chi_{orb} = \chi_{orb\parallel} - \chi_{orb\perp}$, are listed in Table 2. For completeness, the table contains also an estimate of the Langevin diamagnetism of filled shells $\chi_{dia}$ which appears to be close to a free-ionic diamagnetic susceptibility [18,19].

In addition, the enhanced Pauli spin contribution to the magnetic susceptibility was also calculated within the Stoner model:

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

Table 2. Calculated bulk modulus $B$ and contributions to the magnetic susceptibility of $CrB_2$ in PM state (see text for details)

| $B$, Mbar | $\chi_{ston}$ | $\overline{\chi}_{spin}$ | $\overline{\chi}_{orb}$ | $\Delta\chi_{orb}$ | $\chi_{dia}$ | $\chi_{sum}^a$ |
|---|---|---|---|---|---|---|
| | $10^{-4}$ emu/mol | | | | | |
| 2.30 | 4.0 | 7.03 | 0.60 | 0.010 | –0.10 | 7.53 |

$\chi_{sum}^a = \overline{\chi}_{spin} + \overline{\chi}_{orb} + \chi_{dia}$

where $\chi_P = \mu_B^2 N(E_F)$, $S$ is the Stoner enhancement factor, and $\mu_B$ is the Bohr magneton. The Stoner integral $I$, describing the exchange-correlation interaction of the conduction electrons, can be expressed in terms of the calculated parameters of the electronic structure [20,21]:

$$I = \frac{1}{N(E_F)^2} \sum_{qll'} N_{ql}(E_F) J_{qll'} N_{ql'}(E_F). \qquad (3)$$

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

$$J_{ll'} = \int g(\rho(r)) \phi_l(r)^2 \phi_{l'}(r)^2 dr, \qquad (4)$$

where $\phi_l(r)$ are the partial wave functions, and $g(\rho(r))$ is a function of the charge density [16]. The calculated value of the enhanced Pauli susceptibility $\chi_{ston}$ is presented in Table 2 and appears to be lower than the field-induced spin susceptibility $\chi_{spin}$, evaluated by using the full Zeeman term (1). It should be noted, that the field-induced and Pauli spin susceptibilities in Table 2 were calculated for the equilibrium unit cell volume $V_{th}$.

## 4. Discussion

In $CrB_2$ the main contribution to $N(E_F)$ comes from $d$ states of Cr, and the Stoner criterion is nearly fulfilled due to the large value of $N(E_F)$ (see Fig. 4). The calculated susceptibility enhancement factor $S = [1 - IN(E_F)]^{-1}$ appears to be about 8, which is comparable with earlier estimations ($S \simeq 9$ [7]). In the PM phase of $CrB_2$ the magnetic susceptibility rises with decreasing temperature and becomes $\chi_{exp} \simeq 6.5 \cdot 10^{-4}$ emu/mol at $T = 90$ K. The extrapolated PM susceptibility $\chi_{exp}(T \to 0)$ provides the estimation $\chi_{exp}(0) \simeq 7.3 \cdot 10^{-4}$ emu/mol, which is in agreement with the calculated paramagnetic contributions $\chi_{spin}$ and $\chi_{orb}$ from Table 2. The calculated small value of the magnetic anisotropy in $CrB_2$ (less than 1%) is also in line with the experimental data of Ref. 4.

The total susceptibility of metallic systems in the absence of spontaneous magnetic moment can be expressed as the sum ([15,19]):

$$\chi_{tot} = \chi_{spin} + \chi_{orb} + \chi_{dia} + \chi_L, \qquad (5)$$

which, along with the above mentioned contributions, also includes the diamagnetism of conduction electrons $\chi_L$. A rigorous calculation of $\chi_L$ is rather difficult problem for a complicated band structure (see, e.g., [22]), and the free-electron Landau limit is often used for estimations, though for many systems this crude approximation was found not to provide even the correct order of magnitude of the diamagnetic susceptibility. In fact, the agreement of the contributions to the magnetic susceptibility $\chi_{sum} = \overline{\chi}_{spin} + \overline{\chi}_{orb} + \chi_{dia}$ calculated here (see Table 2) with the experimental value of $\chi$ (Table 1) gives evidence that for $CrB_2$ the diamagnetic contribution $\chi_L$ is presumably negligible as compared with the dominating spin contribution $\chi_{spin}$.

In order to analyse the experimental data on pressure effect in the magnetic susceptibility, the volume dependencies of the paramagnetic contributions to susceptibility $\chi_{spin}$ and $\chi_{orb}$ are calculated *ab initio* within the field-induced FP-LMTO technique. The evaluated volume derivative $d \ln(\chi_{spin} + \chi_{orb})/d \ln V = 4.0$ appears to be in agreement with the experimental result for the PM phase of $CrB_2$, $d \ln \chi/d \ln V = 3.8 \pm 0.5$ (see Table 1). It should be pointed out that the calculated value of the pressure effect on $\chi$ is predominately determined by the enhanced spin contribution $\chi_{spin}$.

The measured pressure derivative of the magnetic susceptibility $d \ln \chi/dP$ can be used to derive the spontaneous volume change in $CrB_2$ due to the antiferromagnetic ordering $\Delta V/V \equiv \omega_m$ which relates to the squared local magnetic moment $M^2(T)$ ([23]):

$$\omega_m(T) = \frac{C}{B} M^2(T). \qquad (6)$$

Here $B$ is the bulk modulus, $C$ is the magnetoelastic coupling constant. The latter can be determined within the phenomenological relation [24]:

$$\frac{C}{B} = -\frac{1}{2\chi V_m} \frac{d \ln \chi}{dP}, \qquad (7)$$

where $\chi$ and $V_m$ are the molar susceptibility and volume, respectively. By using in Eq. (7) the experimental values of $\chi$ and $d \ln \chi/dP$ from Table 1 and $V_m = 14.1$ cm$^3$, one estimates the magnetoelastic constant to be temperature independent within experimental errors and equal to: $C/B = (1.07 \pm 0.15) \cdot 10^{-10}$(emu/mol)$^{-2}$. The substitution of the evaluated $C/B$ value and the experimental magnetic moment $M(0) \simeq 0.5 \mu_B/$Cr [5] in Eq. (6) yields the volume change under the AFM transition to be $\omega_m(0) \simeq (0.083 \pm 0.012)$%. This estimate agrees closely with the experimental value $\omega_m(0) = 0.085$% [25].

The pressure dependence of the Néel temperature can be examined in line with a phenomenological approach of Ref. 26, which has been applied to the AFM chromium:

$$T_N \simeq \exp\left(-1/\lambda\right), \qquad (8)$$

where $kT_B$ is of the order of the $d$-band width, and $\lambda \propto IN(E_F)$. The volume dependence of the Stoner product $IN(E_F)$ can be obtained according to Eq. (2), which gives

$$\frac{d \ln \chi}{d \ln V} = \frac{d \ln N(E_F)}{d \ln V} + (S-1)\frac{d \ln[IN(E_F)]}{d \ln V}. \qquad (9)$$

By substituting the experimental data on $d \ln \chi / d \ln V$ from Table 1 into Eq. (9) together with our estimates $d \ln N(E_F)/d \ln V = 1.52$ and $S \simeq 8$, we obtain

$$\frac{d \ln[IN(E_F)]}{d \ln V} \simeq 0.3, \qquad (10)$$

which means a substantial cancellation of the volume effects on the density of states at the Fermi level and the exchange parameter in the Stoner product $IN(E_F)$ of $CrB_2$. Therefore, according to Eq. (8), the effect of pressure on $T_N$ is mainly determined by the band width behavior, $d \ln T_N /dP \approx d \ln T_B /dP$, and appears to be rather small and positive in sign. This is consistent with the measured weak pressure dependence of the Néel temperature in $CrB_2$ ($dT_N /dP = (0.1 \pm 0.1)$ K/kbar). It should be noted, that such behavior of $T_N$ differs essentially from that for pure chromium, where the strong suppression of the AFM state under pressure with $dT_N /dP \simeq -5.1$ K/kbar has been reported [26]. Therefore we can presume, that a different mechanism of the magnetic ordering takes place in $CrB_2$ as compared to the AFM chromium.

To shed more light on the nature of the magnetic ordering in $CrB_2$, the electronic structure calculations for its low temperature helical magnetic structure are required. Such calculations are extremely difficult to perform, and in the present work the spin-polarized electronic structure calculations are carried out for the ferromagnetic phase of $CrB_2$. These calculations provided the spontaneous magnetic moment of $0.8 \mu_B$, in a reasonable agreement with the experiment [5].

## 5. Conclusions

For the first time the pressure effect on the magnetic susceptibility of $CrB_2$ is measured at temperatures both above and below $T_N = 87$ K, and it is found to be almost independent on the magnetic state of the sample. Based on the obtained pressure derivative of the magnetic susceptibility, we evaluated the magnetoelastic coupling constant, which appears to describe correctly the reported spontaneous volume change in $CrB_2$ due to the antiferromagnetic ordering. The measured pressure effect on

the Néel temperature is found to be considerably smaller than that for the pure AFM chromium, and this indicates that different mechanisms govern magnetic ordering in $CrB_2$ and Cr.

It is found that the Stoner approach underestimates substantially the spin susceptibilty for the PM phase of $CrB_2$. This is presumably related to deficiency of the Stoner approach, when both parameters involved in the susceptibility enhancement, $N(E_F)$ and $I$, are calculated and averaged over the band states separately. It should be noted that such response function as $\chi$ is microscopically not uniform in space, and induced magnetization density varies considerably within the unit cell. On the other hand, our *ab initio* calculations in an external magnetic field provided the main contributions to the magnetic susceptibility of $CrB_2$ and allowed to describe the large value of $\chi$ and the magneto-volume effect $d \ln \chi / d \ln V$ in agreement with the experiment.

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