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## PRESSURE EFFECTS ON ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF ANISOTROPIC METALLIC COMPOUNDS

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*Pressure effects on electronic structure and magnetic properties of anisotropic metallic materials ( $\text{CrB}_2$ ,  $\text{FeGe}_2$ ,  $\text{LaFeAsO}$ ) are investigated. Magnetic susceptibilities of  $\text{CrB}_2$  and  $\text{FeGe}_2$  compounds were studied under hydrostatic pressure at fixed temperatures, 77 and 300 K. In order to analyze the experimental magnetovolume effects, the electronic structures were calculated ab initio in external magnetic field as a function of atomic volume by employing a full-potential LMTO method. The calculated field-induced magnetic moments and their volume derivatives compare favorably with the experimental pressure effects in magnetic properties of  $\text{CrB}_2$  and  $\text{FeGe}_2$ . The main role of pressure in high- $T_c$  superconductivity of  $\text{LaFeAsO}$  is found to reduce density of states at the Fermi level and to suppress ferromagnetic spin fluctuations.*

### Introduction

The discovery of high- $T_c$  superconductivity in  $\text{MgB}_2$  and ferropnictides ( $\text{RFeAsO}$ ,  $\text{LiFeAs}$ ,  $\text{AFe}_2\text{As}_2$ ), charge density waves in  $\text{NbSe}_2$ , intriguing magnetic properties of borides and germanides have initiated considerable interest in electronic structure and properties of compounds of transition metals with metalloids and nonmetals. The properties of metalloids themselves are between metals and nonmetals, and when involved in chemical bonding, the metalloids also exhibit middle-of-the-road qualities. They are capable of taking electrons from most metals and will readily lose electrons to most nonmetals. Their electronegativity values are also mid-range. Consequently, it is unlikely for them to be involved in ionic bonding, and it is believed they will establish covalent bonding when found in compounds.

On the other hand, under high pressure a metallic behavior of such compounds often becomes more pronounced, and such a pressure effect can provide drastic changes in electronic and magnetic properties. In this contribution we report results of theoretical and experimental studies of pressure effects on electronic spectra and magnetic properties of selected anisotropic compounds with outstanding physical properties: CrB<sub>2</sub>, FeGe<sub>2</sub> and LaFeAsO.

### Experimental and theoretical details

For certification of the samples quality, the magnetic susceptibility  $\chi$  was measured as a function of temperature using a Faraday microbalance method. The pressure effect on the susceptibility was measured under helium gas pressure up to 2 kbar at fixed temperatures, 77.3 and 300 K, using a pendulum-type magnetometer placed into the nonmagnetic pressure cell [1], and the experimental dependencies  $\chi(P)$  for CrB<sub>2</sub> and FeGe<sub>2</sub> clearly demonstrated linear behavior over the range 0–2 kbar.

The polycrystalline sample of CrB<sub>2</sub> was initially prepared by arc-melting of the stoichiometric amounts of Cr and B elements of better than 99.8% purity in a water cooled crucible under protective argon atmosphere. The study of X-ray powder diffraction revealed that the sample has the AlB<sub>2</sub>-type hexagonal crystal structure, and obtained data on the lattice parameters agree closely with that published in literature. In this work we used the same single-crystalline sample of FeGe<sub>2</sub> as in the magnetostriction studies of Ref. [2]. The susceptibility measurements were performed for magnetic fields in the basal plane and along [001] direction, and the averaged  $\chi$  values were compared with theoretical calculations.

*Ab initio* calculations of the volume dependent electronic structures were performed by employing a modified full-potential relativistic LMTO method (FP-LMTO) [3,4] for nonmagnetic, ferromagnetic (FM), and antiferromagnetic (AFM) phases of studied compounds in the LSDA approximation of the density functional theory. No shape approximations were imposed on the charge density or potential, what is especially important for the open and anisotropic crystal structures.

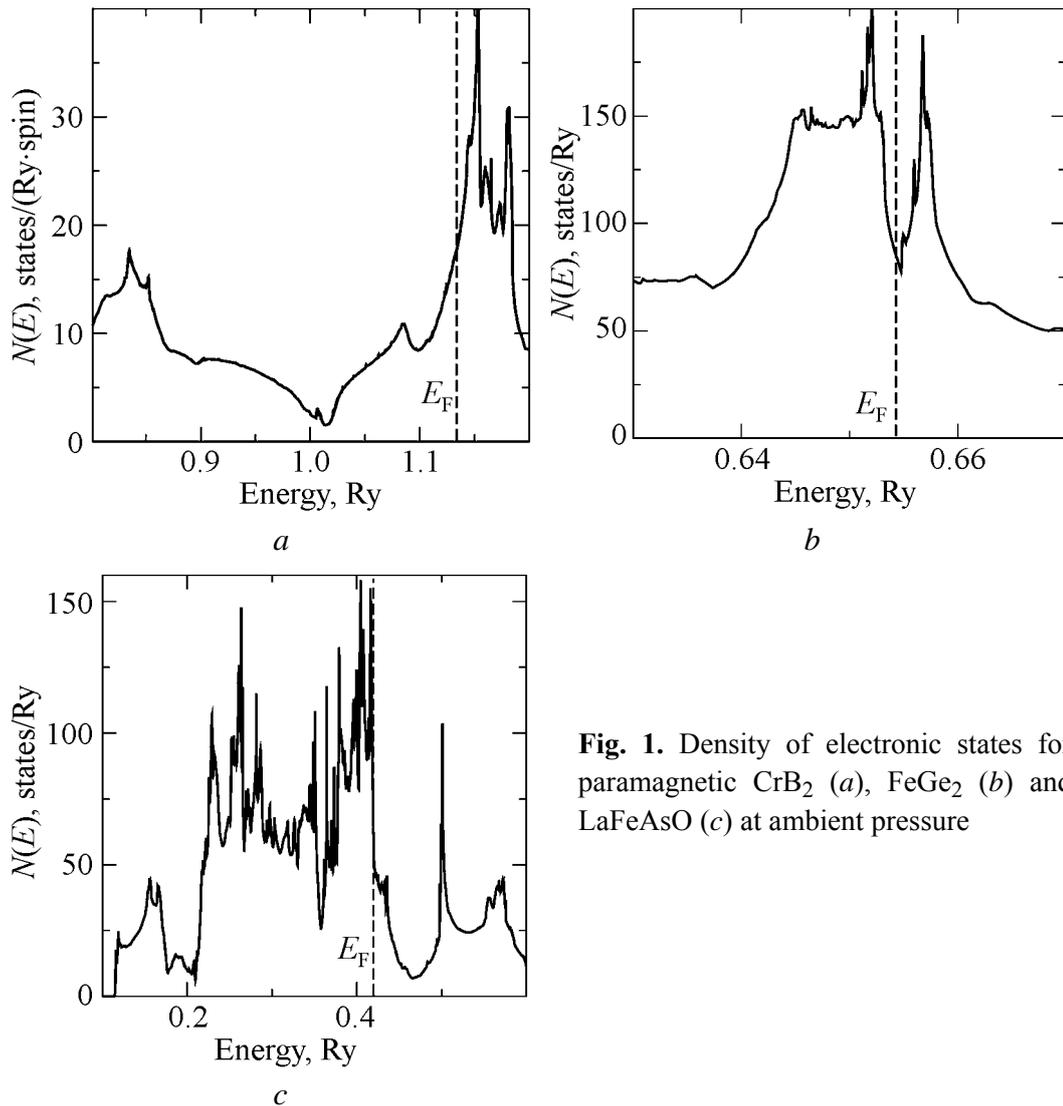
To analyze the observed magnetovolume effect values, the magnetic susceptibility and its volume dependence were evaluated by means of the Zeeman operator,  $H(2\hat{s} + \hat{1})$ , incorporated in FP-LMTO Hamiltonian for calculations of the field-induced spin and orbital magnetic moments. The corresponding contributions to  $\chi$  were derived from the field-induced moments, which have been calculated in an external magnetic field of 10 T.

### CrB<sub>2</sub>

CrB<sub>2</sub> is an itinerant-electron antiferromagnet with the Néel temperature  $T_N = 85\text{--}88$  K [5–7], possessing a hexagonal structure of AlB<sub>2</sub> type. The neutron diffraction studies revealed a complicated helicoidal magnetic structure of CrB<sub>2</sub>, with magnetic moment of about  $0.5\mu_B$  per Cr atom (at  $T = 0$ ) turning in  $a$ - $c$  plane [6]. The sus-

ceptibility of CrB<sub>2</sub> in the PM phase is an order of magnitude higher than that of other diborides, presumably demonstrating a large exchange-enhancement effect.

The band structure calculations revealed that *p*-*d* hybridization and filling of the conduction band are predominantly responsible for properties of transition metal diborides. As is seen in Fig. 1,*a*, in CrB<sub>2</sub> the Fermi level  $E_F$  lies at the steep slope of the  $N(E)$  peak where DOS rapidly grows with energy, and the main contribution to  $N(E_F)$  comes mostly from *d*-states of Cr. The Stoner criterion is nearly fulfilled for CrB<sub>2</sub>, and the calculated susceptibility enhancement factor  $S$  appeared to be about 8, which is comparable with earlier estimations ( $S \approx 10$ , [8]).



**Fig. 1.** Density of electronic states for paramagnetic CrB<sub>2</sub> (*a*), FeGe<sub>2</sub> (*b*) and LaFeAsO (*c*) at ambient pressure

The magnetic susceptibility of CrB<sub>2</sub> decreases linearly with pressure at both temperatures, and the corresponding pressure derivatives,  $d \ln \chi / dP$ , are listed in Table together with the values of  $\chi$  measured at ambient pressure. In order to convert the pressure derivative into the volume derivative, we used the calculated bulk modulus value,  $B = 2.3$  Mbar. A moderate value of the pressure effect is

found to be negative in sign and weakly dependent on the magnetic state of the compound. The main contributions to  $\chi$  and their volume dependences are calculated *ab initio*, and appeared to be in close agreement with experimental data (see Table). In addition, the measured pressure dependence of the Néel temperature,  $dT_N/dP = 0.1 \pm 0.1$  K/kbar, differs essentially from that for pure Cr where the strong suppression of the AFM state under pressure with  $dT_N/dP \simeq -5.1$  K/kbar has been reported [9].

Table

Magnetovolume effects in CrB<sub>2</sub>, FeGe<sub>2</sub> and LaFeAsO

| Compound          | T, K | $\chi, 10^{-3}$ emu/mole |            | $d\ln\chi/dP, \text{Mbar}^{-1}$ |               | $d\ln\chi/d\ln V$ |            | $d\ln N(E_F)/d\ln V$ |
|-------------------|------|--------------------------|------------|---------------------------------|---------------|-------------------|------------|----------------------|
|                   |      | exp                      | theor (PM) | exp                             | exp           | theor (PM)        | theor (PM) |                      |
| CrB <sub>2</sub>  | 77.3 | 0.642                    | –          | $-1.82 \pm 0.3$                 | $4.2 \pm 0.7$ | –                 | –          | –                    |
|                   | 300  | 0.511                    | 0.7        | $-1.65 \pm 0.2$                 | $3.8 \pm 0.5$ | 4                 | 1.5        | –                    |
| FeGe <sub>2</sub> | 77.3 | 2.7                      | –          | $-2.73 \pm 0.3$                 | $4.6 \pm 0.5$ | –                 | –          | –                    |
|                   | 300  | 1.7                      | 2          | $-2.23 \pm 0.3$                 | $3.8 \pm 0.5$ | 4.5               | 1.6        | –                    |
| LaFeAsO           | 30   | 0.5 [16]                 | 0.6        | –                               | –             | 6                 | 1.9        | –                    |

The measured pressure derivative of the susceptibility,  $d\ln\chi/dP$ , can be used to evaluate the spontaneous volume change in CrB<sub>2</sub> due to the AFM ordering:

$$\frac{\Delta V}{V} \equiv \omega_m = \frac{C}{B} M^2(T), \quad (1)$$

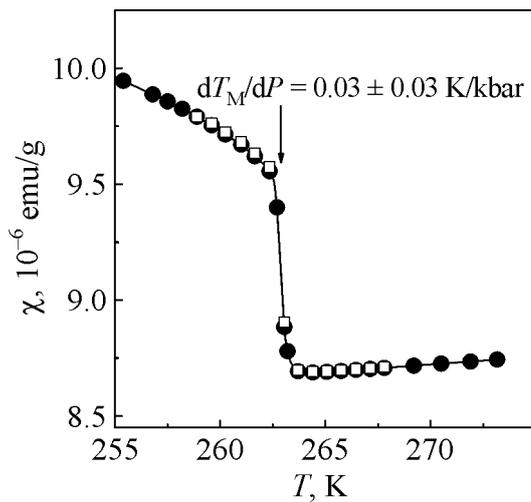
where  $C$  is the magnetoelastic coupling constant,  $B$  – the bulk modulus,  $M^2(T)$  – the squared local magnetic moment. According to the phenomenological relation [10]:

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

where  $\chi$  and  $V_m$  are the molar susceptibility and volume, respectively. Using in Eq. (2) the experimental values from the Table and the calculated  $V_m = 13.8 \text{ cm}^3$ , we estimated the magnetoelastic constant as:  $C/B = (1.1 \pm 0.1) \cdot 10^{-10} (\text{emu/mole})^{-2}$ . The substitution in Eq. (1) of the above  $C/B$  value and experimental value of the magnetic moment,  $M(0) \simeq 0.5 \mu_B/\text{Cr}$  [6], gives the volume change at  $T = 0$  to be  $\omega_m(0) \simeq 0.086\%$ . This estimate agrees closely with the experimental value of  $\omega_m(0) = 0.085\%$  [11].

### FeGe<sub>2</sub>

FeGe<sub>2</sub> is an itinerant electron antiferromagnet of tetragonal C16-type crystal structure that has a second-order transition from a PM phase to an incommensurate (IC) phase at 289 K with a long-wavelength modulation in the basal plane, and the other first-order transition from an IC to a commensurate AFM phase at  $T_M = 263$  K [2,12]. Nearest-neighbour (NN) Fe atoms are along the  $c$ -axis and their moments have FM alignment, whereas the next-NN Fe atoms are along the [110] direction with AFM alignment of the moments below  $T_M = 263$  K [13].



**Fig. 2.** Temperature dependencies of the magnetic susceptibility of FeGe<sub>2</sub> around  $T_M = 263$  K in magnetic field 17 kOe applied along [100] axis for two different pressures: ● –  $P = 0$ , □ –  $P = 1.6$  kbar. The higher pressure data are shifted upwards to about  $0.045 \cdot 10^{-6}$  emu/g for convenience of comparison

According to our calculations, the electronic structure at  $E_F$  is governed by a strong hybridization of the  $3d$  (Fe) and  $4p$  (Ge) states, which leads to a peculiar structure of DOS with the Fermi level located at the V-shaped minimum of  $N(E)$  (see Fig. 1,*b*). FeGe<sub>2</sub> has a Fermi surface driven instability which forces it into an incommensurate spin density wave state [13,14]. The calculated bulk modulus,  $B_{\text{theor}} = 1.7$  Mbar, is in reasonable agreement with the reported experimental value,  $B_{\text{exp}} = 1.5$  Mbar [12].

The measured pressure effect on the  $T_M$  temperature,  $dT_M/dP = 0.03 \pm 0.03$  K/kbar was found to be weak (see Fig. 2). As is seen in the Table, the  $d \ln \chi / dP$  derivatives appeared to be close both in PM and AFM phases of FeGe<sub>2</sub>. In order to convert the pressure derivatives into the volume derivatives, we used the calculated bulk modulus,  $B = 1.7$  Mbar. The spin and Van Vleck contributions to  $\chi$  and their volume dependences for the PM phase were calculated *ab initio* and were found in agreement with the experimental data in the Table. It should be noted that  $d \ln \chi / dV$  derivatives in the itinerant AFM compounds CrB<sub>2</sub> and FeGe<sub>2</sub> are somewhat lower than the corresponding derivatives in the PM compounds with highly enhanced spin susceptibility (CeCo<sub>2</sub>, YCo<sub>2</sub>, TiCo, Ni<sub>3</sub>Al [15]).

### LaFeAsO

Reported superconductivity (SC) up to 54 K in  $R\text{FeAsO}$  ( $R = \text{La, Pr, Nd, Sm, Gd}$ ) [16,17] has raised a number of questions about the nature of SC state and the pairing mechanism, and encouraged the studies of high- $T_c$  superconductors outside the cuprate family. The tetragonal structure of  $R\text{FeAsO}$  exhibits strong two-dimensional features, and SC is presumably confined to the Fe–As layers. Simple chemical considerations suggest that their formula can be represented as  $R^{+3}O^{-2}Fe^{+2}As^{-3}$ , which is consistent with the observed semi-metallic properties and spin-density waves in LaFeAsO below 150 K [17]. Actually, in  $R\text{FeAsO}$  the high- $T_c$  SC has been achieved with F-doping, and a competition is anticipated between the spin ordering and SC [16,17].

The band structure of LaFeAsO is determined by hybridization of  $d$  (Fe) and  $p$  (As) states within the Fe–As layers. As is seen in Fig. 1,  $c$ , the Fermi level is located at the steep slope of  $N(E)$ . The DOS at  $E_F$  comes essentially from the  $d$ -electrons of Fe, and the partial contributions of other states are substantially smaller. Also, the LaFeAsO compound is found to be on the verge of magnetic instability, very close to the FM quantum critical point. Though the calculated Stoner enhancement factor  $S \simeq 5$  provides a high spin magnetic susceptibility, it nevertheless can not describe fully the experimental value ( $\chi \simeq 5 \cdot 10^{-4}$  emu/mole, [17]). On the other hand, the susceptibility calculated in external magnetic field appeared to be very close to the experimental value at the theoretical lattice parameter. The Van Vleck contribution to  $\chi$  comes mainly from  $d$ -electrons of Fe and amounts up to 10% of total susceptibility.

The experimental susceptibility in LaFeAsO compound is large with relatively flat temperature dependence, whereas upon F-doping it grows further and becomes Curie–Weiss like above  $T_c$  [17]. Our FP-LMTO calculations for the F-doped LaFeAsO, which were performed using the virtual crystal approximation, indicate that the main function of doping is to shift the system away from FM instability. This was proved by calculating the Stoner product  $IN(E_F)$ , where  $I$  is the exchange parameter. In the same way, the total DOS  $N(E_F)$  is also found to be decreasing with pressure, as well as the enhanced Pauli susceptibility (see the Table).

Based on the experimental observations, a suggestion was put forward [17,18] that SC state in LaFeAsO is favored by the AFM spin fluctuations (SF). There is a growing evidence that electron-phonon interaction is too small in the pure and F-doped LaFeAsO to provide the conventional SC [18]. It should be noted that in the undoped LaFeAsO the calculated susceptibility is larger, and the experimental one is smaller than in the doped systems. This suggests that besides FM spin fluctuations there are also other important spin excitations in RFeAsO.

At the moment we can suggest that the spectrum and relative distribution of SF in RFeAsO can arise from different sources. Firstly, the Fe–As–Fe positions angle is larger than  $90^\circ$  and provides a possibility of AFM superexchange interaction via the As  $p$  orbitals [19]. Furthermore, a substantial direct Fe–Fe overlap in Fe–As planes can yield an additional AFM exchange. Also, the calculated band structure indicates a possibility of the nesting-related AFM spin-density-wave type SF. Further analysis of AFM interactions in RFeAsO requires a detailed study of the magnetic response and fine band structure features at the Fermi level.

### Conclusions

The pressure effect on the AFM ordering temperatures of CrB<sub>2</sub> and FeGe<sub>2</sub> is found to be much weaker than in the itinerant AFM chromium. For both compounds the pressure derivatives of  $\chi$  have been measured for the first time. Based on these  $d \ln \chi / dP$  derivatives, the estimate of the magnetoelastic coupling constant describes properly the spontaneous volume change in CrB<sub>2</sub> due to the AFM ordering.

It is found that the Stoner approach substantially underestimates the spin susceptibility for PM phases of CrB<sub>2</sub>, FeGe<sub>2</sub> and LaFeAsO, whereas the calculated field-induced spin and orbital moments allowed to describe the large  $\chi$  and magnetovolume effects in these compounds, which are close to the quantum critical point. This is presumably related to deficiency of the Stoner approach, when both parameters involved in susceptibility enhancement,  $N(E_F)$  and  $I$ , are calculated and averaged over the band states separately. On the other hand, such response function as  $\chi$  is microscopically not uniform in space, and induced magnetization density varies considerably within the unit cell.

Our calculations for LaFeAsO indicate that the main role of pressure (and F-doping) is to shift the system away from the FM instability, which is expected to be unfavorable for SC, and to suppress FM spin fluctuations.

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