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2001 J. Phys.: Condens. Matter 13 11661

(http://iopscience.iop.org/0953-8984/13/50/325)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 11661–11667 PII: S0953-8984(01)27745-5

Electronic structure and electric field gradient in MgB_2 under pressure: an *ab initio* study

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Received 9 August 2001, in final form 28 September 2001
Published 30 November 2001
Online at stacks.iop.org/JPhysCM/13/11661

Abstract

We report here *ab initio* density functional theory study of the electronic band structure and electric field gradient (EFG) in MgB_2 under pressure. The band structure calculations are in agreement with other recent calculations. The superconductivity in MgB_2 is related to and dominated by the existence of boron σ $p_{x,y}$-band holes at the Γ point, with negligible contribution from the Mg ions. The character of the σ band is unchanged even after application of pressure, although there is a shift of position and an increase of dispersion. The calculated density of states decreases with pressure which, in conjunction with the Bardeen–Cooper–Schrieffer theory, agrees with the trend of the experimental T_c versus pressure data. The broad bump in $T_c(P)$ data observed by Tissen *et al* near 9 GPa is not indicated in the present band structure study. The EFG at the B site is nearly constant as a function of pressure and that of Mg changes by ∼34% over the pressure range considered. The present result indicates that the B electronic system does not change much under pressure up to ∼38 GPa, which confirms one reported study but disagrees with the other.

1. Introduction

Recent discovery of superconductivity in the non-cuprate intermetallic MgB_2 at 39 K [1] has aroused much interest in the scientific community. A variety of experimental [2–13] and theoretical [14–30] research has been carried out to find out its structural, elastic, electronic and other properties. A few of these works involve both theoretical and experimental studies. Some discussions of electronic band structure have already been made in a number of these works that reveal that there are two distinct types of band contributed by boron. Among these the two-dimensional holelike B σ bands arise from intraplanar $p_{x,y}$-like orbitals and give a flat DOS with a prominent van Hove spike. A weaker three-dimensional p_z-like band also contributes to the DOS.

High-pressure studies show that the transition temperature T_c decreases with increasing pressure [4, 5, 10, 28]. Compression decreases both lattice constants a and c. This would indicate a possible way of searching for higher T_c material. The lattice parameters are expected

to have considerable effect on the B σ band. The study of Wan *et al* [25] has indicated that increasing the lattice constant along the c axis would increase the density of states (DOS) at the Fermi level. This causes an upward shift of the σ band and thereby increases the hole number in the band, which leads to an increase of T_c. This can be done by making MgB_2 have a larger c axis and shorter a (or b) axis by doping.

The peculiarities of electronic structure and chemical bonding are connected with the electric field gradient (EFG). This is directly related to the quadrupole charge distribution of the electron density around the probe nucleus. The measured quadrupole interaction can be interpreted on the basis of EFG [27]. Thus theoretical study of EFG of MgB_2 constitutes an important exercise that can lead to reliable interpretation of the observed data and to relate this with the specific features of the electronic structure and bonding.

Very recently Tissen *et al* [10] observed an interesting feature in the pressure dependence of T_c. They reported a broad bump near 9 GPa, which they speculated to arise from a pressure-induced electronic Lifshitz transition. These authors also indicated that existing band structure calculations of MgB_2 lend some support for such an explanation. On the other hand Deemyad *et al* [13] reported a monotonic decrease of T_c with pressure right up to 20 GPa. Further there are two conflicting points of view regarding the change of B $p_{x,y}$ occupancy under pressure. Vogt *et al* [9] conclude that B $p_{x,y}$ occupancy is altered by pressure, in contrast to the B p_z states. On the other hand Medvedeva *et al* [27] disagree with this conclusion. They found small changes in the dispersion and location of the B $p_{x,y}$ bands of MgB_2 under pressure. They conclude that no large changes take place under pressure in (i) the partial B p occupations, (ii) boron EFG and hence (iii) boron electronic structure. A further investigation on the observation made by Tissen *et al* [10] and also the important question with opposing viewpoints by Vogt *et al* [9] and Medvedeva *et al* [27], respectively, is desirable. Although theoretical investigations of the band structure of MgB_2 have been carried out by several authors [15, 17, 19, 21, 25, 26, 29] only two groups [8, 27] reported results on both the electron band structure and EFG. Neither of these two papers, however, discussed both the above-mentioned issues together. Medvedeva *et al* [27] used the full-potential linear muffin-tin orbital generalized gradient approximation (FLMTO–GGA) only to study band structure and EFG but they did not discuss the bump structure in $T_c(P)$. It would thus be interesting to utilize a different *ab initio* approach to examine and shed further light on the issues in question.

2. Method of calculations

We use the self-consistent-field Hartree–Fock linear combination of atomic orbital (SCF-HF-LCAO) computer program CRYSTAL98 [31]. *A posteriori* density functional (DFT) correlations to the HF results for the total energy are included, with the correlation and exchange functions proposed by Perdew and Zunger [32] and Becke [33], respectively. The basis sets used are 6-21G* and 8-61G for B and Mg, respectively. The exponents of the most diffuse sp and d shells for each atom have been optimized by searching for the minimum crystalline energy. The quality of the calculation depends on the density of points with which the Brillouin zone (BZ) is sampled. The integrations over the BZ were performed using the Monkhorst–Pack scheme [34]. To ensure convergence for the BZ integration with accuracy very tight tolerances were utilized in the evaluation of the infinite Coulomb and exchange series. A dense Gilat net [35] was defined with a total of 793 k-points in the reciprocal space, corresponding to a shrinkage factor of 24.

The total energy E of MgB_2 has been calculated at different primitive cell volume (V). The energy was minimized as a function of c/a ratio for selected values of volume. The zero pressure bulk modulus B_0 and its pressure derivative B_0' were determined by fitting the Murnaghan equation of state as detailed elsewhere [22]. The pressure was then obtained from

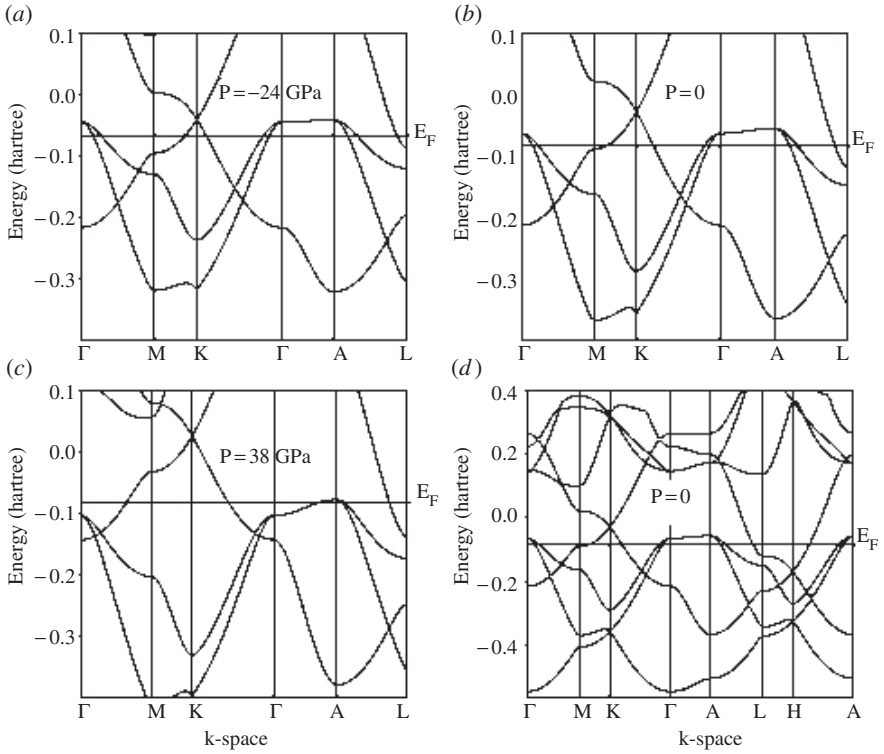

Figure 1. Band strucutre of MgB_2 (*a*) after expansion ($V_n = 1.096$, $P = -24$ GPa); (*b*) at equilibrium ($P = 0$); (*c*) under pressure ($V_n = 0.85$, $P = 38$ GPa) and (*d*) at equilibrium but over a wider energy range and along additional symmetry directions.

the normalized primitive-cell volume, $V_n (= V/V_0$, V_0 being the equilibrium volume) through the thermodynamic relationship $P = B_0(V_n^{-B_0} - 1)/B_0$.

The EFG tensor was calculated directly from the SCF-HF-DFT electron density. The coordinate axes are chosen in such a manner that V_{zz} is the EFG component along the crystallographic c axis. Then the tensor is completely characterized by two parameters: the largest component V_{zz} and the axial asymmetry parameter η defined by $\eta = |V_{xx} - V_{yy}|/|V_{zz}|$.

3. Result and discussion

We first performed detailed SCF-HF-LCAO (DFT) calculations for MgB_2 in its ground state, varying c and a, thus determining the equilibrium volume. It was necessary to perform 20 independent calculations over a range of volumes and c/a ratio. The optimized lattice parameters of MgB_2 are as follows: $a = 3.0889$ Å, $c = 3.5337$ Å. These values are in very good agreement with the measured values: $a = 3.084$ Å and $c = 3.523$ Å [1, 21]. The calculated bulk modulus and elastic constants are reported elsewhere [22, 24]. To examine the effects of volume (and hence pressure) on the electronic band structure near the Fermi level (E_F) we chose the maximum change in V_n in such a way that pressure P lies in the range -25 to 40 GPa. At each volume within the range the structural parameters have been optimized and the energy bands and density of states calculated. The full BZ is spanned in such a way that Γ–M–K–Γ–A–L–H–A directions are covered. The Γ–M–K–Γ lines are in the basal plane, while A–L–H–A lines are on the top of the plane at k_Z. The band structure at the equilibrium volume ($P = 0$) is shown in figure 1(*b*). Figure 1(*d*) shows the result for the band structure calculation

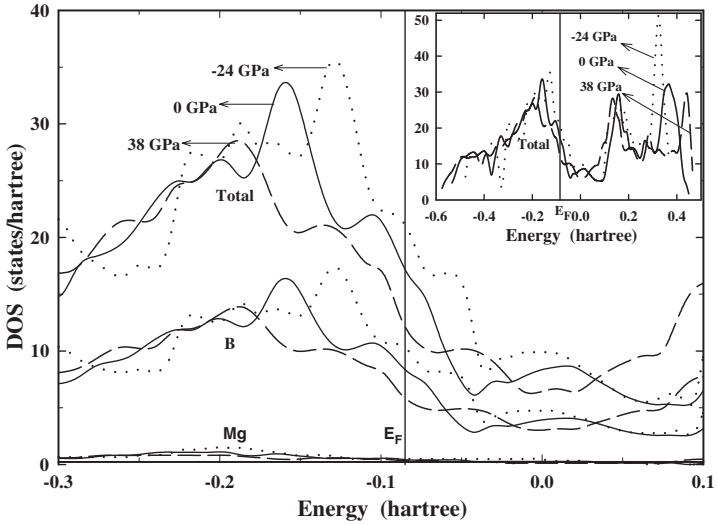

Figure 2. Total and partial electronic density of states (DOS) of MgB_2 as a function of pressure. The inset shows the toal DOS over a wider energy range.

but with a wider energy range and along additional symmetry directions, e.g., L–H–A. There are two distinct types of band, both of which are contributed by boron. The upper part of the valence band is composed of B 2p states which form two sets of bands with $\sigma(2p_{x,y})$ and $\pi(p_z)$ character. The general features of the bands obtained in this paper are in very good agreement with results from other studies [14, 15, 17, 21, 29]. The $\sigma(2p_{x,y})$ band along Γ–A is doubly degenerate, quasi-two-dimensional and makes a considerable contribution to the DOS at E_F for MgB_2. The existence of degenerate $p_{x,y}$ states above E_F at the Γ point in the BZ has been shown to be crucial for superconductivity in MgB_2 [14]. The weaker ppπ-interactions result from B $2p_z$ bands. These 3D-like bands possess maximum dispersion along the Γ–A direction.

The band structure away from equilibrium is shown in figures 1(*a*) and (*c*). The character of the σ band is unchanged even after application of pressure, because the symmetry is not broken. The weak dispersion of the σ band along Γ–A reflects the particular quasi-two-dimensionality. The dispersion increases slightly with increase of pressure. The σ band crosses the Fermi surface at the Γ point at a pressure of ∼38 GPa ($V_n = 0.85$). When the σ band is below the Fermi surface, the σ bonding state is completely filled. Thus compression decreases the holes in the σ band. Neaton and Perali [21] observed that the σ bands of MgB_2 are nearly free-electron-like: their dispersion is parabolic near the Γ point, and their overall bandwidth is comparable to the free electron value (∼15.5 eV). We find the same features and confirm their observation that the bandwidth (∼15 eV) increases as pressure increases in line with that expected for free electrons.

In figure 2 we show the total and partial electronic density of states near the Fermi level as a function of pressure. The inset shows the total DOS over a wider energy range. The shape and locations of the bands shown in figure 1 are reflected in the density of states. The density of states $N(E_F)$ at equilibrium ($P = 0$) is 17.5 states/hartree. The value reduces to 12.5 states/hartree at $P = 38$ GPa. Thus the DOS decreases by as much as 29% over this pressure increase. That the $N(E_F)$ increases as the lattice is expanded is contrary to expectation for a nearly-free-electron metal. The result is in agreement with that of other workers [20, 21, 25]. This observation, via the BCS equation, shows that T_c should decrease

Table 1. V_{zz}^B in 10^{21} V m^{-2} for MgB_2 at equilibrium.

Ref.	V_{zz}^B
Theory	
This	1.50
[8]	1.85
[27]	1.88
Expt	
[7]	1.68
[11]	1.7 ± 0.01
[12]	1.7 ± 0.1

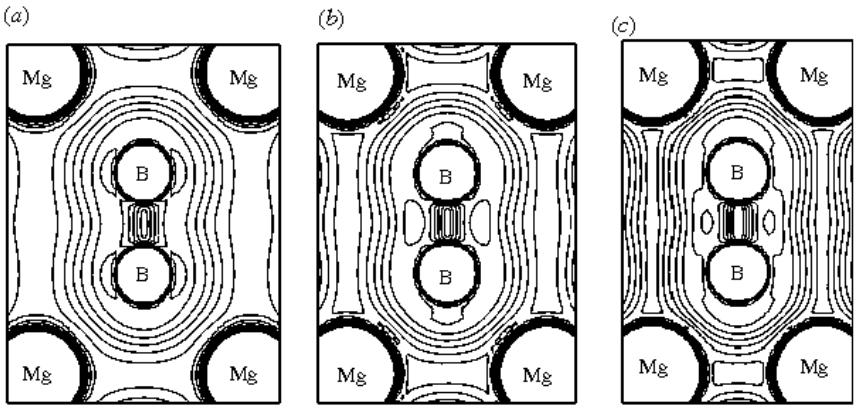

Figure 3. Total electron charge density map on the (110) plane through Mg and B atoms at (*a*) $P = -24$ GPa, (*b*) $P = 0$ and (*c*) $P = 38$ GPa. Isodensity curves are separated by 0.01 Å^{-3}.

with the increase of pressure, a result in agreement with experiment for MgB_2 [10]. Neaton and Perali [21] remarked that the dependence of the DOS on pressure is almost entirely due to the changes in the width and position of a considerable van Hove peak (∼2 eV below the Fermi level). This originates from a saddle point in the highest occupied σ band at the M point. Further the decrease in bandwidth with decreasing pressure reduces the separation between the peak and the Fermi level, enhancing the DOS. The singularity is further enhanced by an increase in two-dimensionality.

A redistribution of carriers between σ and π bands occurs with the increase of pressure, and the number of holes in the σ band decreases, i.e., the top of the band moves down towards E_F and below. The strong electron–phonon coupling results in splitting the σ band into two sub-bands [17]. With application of pressure of 38 GPa the lower sub-band crosses E_F, thereby changing the Fermi surface topology. Tissen *et al* [10] assumed that the Fermi level crosses the van Hove singularity in the DOS at $P \sim 9$ GPa, thereby causing the anomaly in $T_c(P)$ due to the electronic transition. Our calculations do not indicate this to happen at a pressure as low as ∼9 GPa. The results of Deemyad *et al* [13] also support our findings. They measured the dependence of T_c on nearly hydrostatic pressure for an isotopically pure (^{11}B) MgB_2 sample. The analysis of $T_c(P)$ data to 20 GPa demonstrates that the monotonic decrease of T_c with pressure arises predominantly from the decrease in the coupling constant λ due to lattice stiffening, and not from electronic effects.

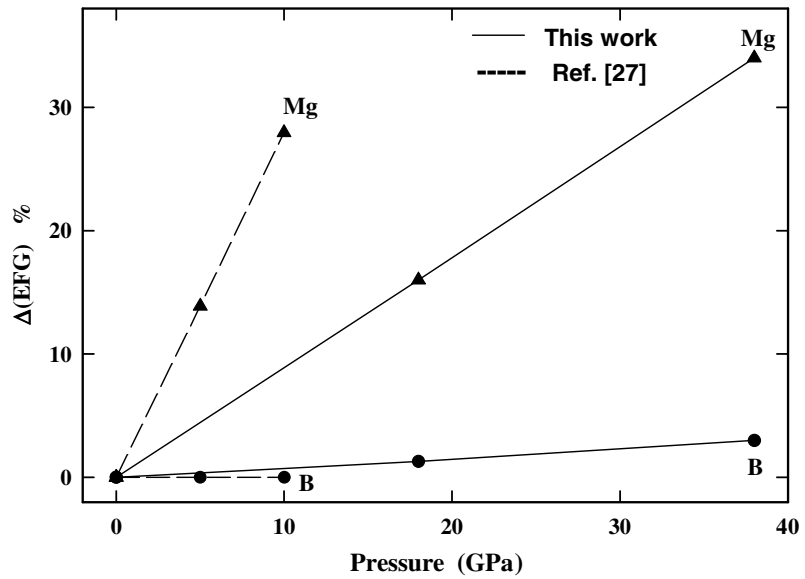

Figure 4. Percentage change of the values of EFG at B and Mg sites as a function of pressure.

The total charge densities of MgB_2 at different pressures for the (110) plane are shown in figure 3. Mg nuclei are located at the corners of the charge density map and B nuclei are at the $(1/3, 1/2)$ and $(2/3, 1/2)$ positions. The density profile at zero pressure (figure 3(b)) shows similar features to that in [20]. A low electron accumulation between Mg and B is indicated. Further the electron population in the Mg site is much lower than that for a neutral Mg atom. These indicate an ionic bonding between Mg and B. On the other hand there is a strong covalent bonding between B–B atoms. This is evident from the maximum charge density (with a strongly aspherical character) at the bond middle. A somewhat homogeneous charge distribution between the Mg atoms indicates an appreciable degree of metallic bonding between them. MgB_2 is a mixed bonded solid and the band structure shows features similar to sp metals. The effect of application of pressure on charge density is evident from figure 3(c). There is a moderate transfer of charge from the region between the B ions into the adjacent interstitial region. This is regarded as a transfer from σ to π type bonds [20]. The main features at $P = 38$ GPa are not too different from those at ambient pressure.

The EFG tensor was estimated directly from the SCF-DFT electron density. The principal component of the EFG tensor at the boron site and the Mg site are shown in table 1 together with other available data. The calculated values of EFG at the B site agree well with the available experimental data and theoretical results obtained using different methods [7, 8, 11, 12, 27]. The axial asymmetry parameter η was found to be zero as expected.

The calculated value of EFG at the B site is of the same order of magnitude as V_{zz} at the Mg site and is of opposite sign. No conclusion can be drawn regarding the value of V_{zz} at the Mg site as no experimental value is available. Figure 4 shows the changes of EFG in MgB_2 as a function of pressure. The B EFG is nearly constant up to $\sim$40 GPa, and that of Mg increases rapidly (34% change over the pressure range considered) but at a slower rate compared to that obtained in [27]. The large value of EFG at the B site can be explained by the existence of boron $2p_{x,y}$ hole states as done in [27]. Since the EFG is a sensitive characteristic of the electronic charge distribution, we conclude that there are no large changes in the partial

charges of the B 2p states and boron electronic structure under pressure. This confirms the observation made by Medvedeva *et al* [27] but disagrees with that of Vogt *et al* [9].

Acknowledgments

The authors would like to thank the Ministry of Science and Technology, Government of Bangladesh for financial support. FNI acknowledges the grant of a Scholarship under the Prime Minister's Fund for Research and Higher Studies.

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