Precise tight-binding description of the band structure of MgB_2

D. A. Papaconstantopoulos and M. J. Mehl
Center for Computational Materials Science, Naval Research Laboratory, Washington D.C. 20375-5000
(Received 19 June 2001; published 11 October 2001)

We present a careful recasting of first-principles band-structure calculations for MgB_2 in a nonorthogonal sp-tight-binding (TB) basis. Our TB results almost exactly reproduce our full-potential linearized augmented plane-wave results for the energy bands, the densities of states, and the total energies. Our procedure generates transferable Slater-Koster parameters that should be useful for other studies of this important material.

DOI: 10.1103/PhysRevB.64.172510 PACS number(s): 74.25.Jb, 71.15.Dx

The recent discovery of superconductivity in MgB_2 (Ref. 1) has created great interest in the study of this material, both to understand the mechanism of superconductivity and to explore other properties of MgB_2 and related materials. Intensive research has been carried out both by experimentalists[1–3] and theorists.[4–9] There have been several studies of the electronic structure of MgB_2 including total-energy, band-structure, and phonon-spectra calculations as well as evaluations of the electron-phonon coupling, which seems to have emerged as the prime candidate for explaining the superconducting behavior.

In this paper we present an accurate tight-binding (TB) description of the band structure and total energy of MgB_2. While there have been TB interpretations of the electronic structure of MgB_2 in the literature, a realistic recasting of the details of the first-principles electronic-structure calculations is lacking. Our approach follows the nonorthogonal (NRL) TB methodology,[10,11] which is based on deriving a nonorthogonal TB Hamiltonian by fitting to both the total-energy and energy-band results of a first-principles full-potential linearized augmented plane-wave[12,13] (LAPW) calculation using the Hedin-Lundqvist parametrization of the local-density approximation (LDA).[14] We first performed detailed LAPW calculations for MgB_2 in its ground-state (AlB_2) structure, varying c and a, thus determining the LDA equilibrium volume. It was necessary to perform 17 independent LAPW calculations over a large range of volumes and c/a ratios. Our LAPW equilibrium parameters are $c=6.55$ a.u. and $a=5.75$ a.u., as compared to the experimental values of $c=6.66$ a.u. and $a=5.83$ a.u. As is usually the case, the LDA underestimates the experimental values, here by about 1.5%.

All the above results, i.e., 17 values of the total energy and the energy bands for 76 k points in the irreducible hexagonal Brillouin zone, were used as a database to determine the parameters of our tight-binding Hamiltonian. According to the NRL-TB scheme the on-site parameters depend on the density of the neighboring atoms and the hopping integrals have a polynomial dependence that extends to at least the third nearest-neighbor distance. Our basis included the s and p orbitals in both Mg and B in a nonorthogonal two-center representation. A wave-function analysis of our LAPW results shows that the bands up to the Fermi level ε_F are strongly dominated by the B p states with very little contribution from the Mg ions. It turns out, however, that an accurate TB fit including only the B orbitals is impossible, and therefore the Mg s and p orbitals were included in the fit. Furthermore, to obtain an accurate fit it was essential to block diagonalize the Hamiltonian at the high-symmetry points Γ, A, L, K, and H. We find that at a given set of lattice parameters (c,a) we can reproduce the energy bands of MgB_2 quite well. A comparison is shown in Fig. 1, where the solid and broken lines represent the LAPW and TB bands, respectively, at the LDA values of the equilibrium lattice parameters. The TB bands are in very good agreement with the LAPW bands, including the two-dimensional B-σ band in the $\Gamma\rightarrow A$ direction just above ε_F, which has been identified as hole-band-controlling superconductivity.[5,7] The rms fitting error is 2 mRy for the total energy, and close to 10 mRy for the first five bands. Beyond the fifth band our fit is not as accurate, as the Mg d bands, which are not included in our Hamiltonian, come into play. The values of our TB parameters are given in Table I following the notation of Bernstein *et al.*[15] In this table we also show, for the convenience of the reader, the actual Slater-Koster parameters for three or four nearest neighbors determined from our formulas for the specific LDA equilibrium values of the lattice constants.

In Fig. 2 we show a comparison of TB and LAPW densities of states (DOS). There is an excellent agreement in both the total DOS and the B p-like DOS. To facilitate the comparison we have normalized the muffin-tin decomposed LAPW values so that the contributions from the angular mo-

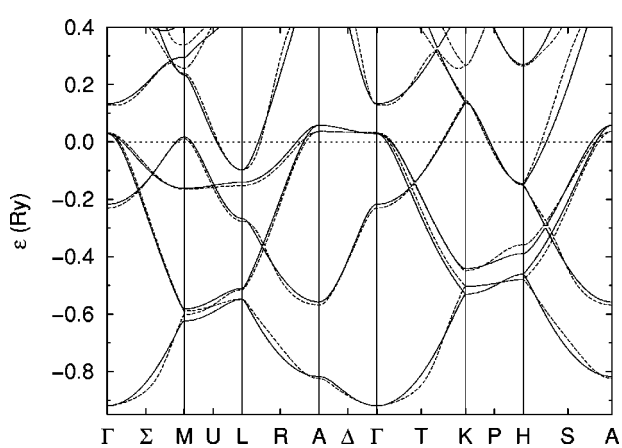

FIG. 1. The band structure of MgB_2 in the AlB_2 structure at the theoretical equilibrium volume, as determined by the full-potential LAPW method (solid lines) and our tight-binding parametrization (dashed lines). The Fermi level is at $\varepsilon=0$.

TABLE I. Tight-binding parameters for MgB_2, generated following the methods of Mehl and Papaconstantopoulos (Ref. 11) and Bernstein *et al.* (Ref. 15). Also shown are the generated Slater-Koster tight-binding parameters for the nearest neighbors at the LDA equilibrium lattice constants, $a=5.75$ a.u. and $c=6.53$ a.u. On-site energies are generated from the ''densities'' of like atoms, that is, the Mg on-site parameters come from the density of Mg atoms, and the B on-site parameters from the density of B atoms. $F(R)$ is the cutoff function from Eq. (2) of Bernstein *et al.* (Ref. 15), with $R_c=12.5$ a.u. and $L_c=0.5$ a.u. All energies are in Rydbergs, all distances in a.u.

Mg-Mg interactions

On-site parameters ($\lambda=0.93961$ a.u.$^{-1/2}$)

$$\rho_{\mathrm{Mg}}=\Sigma_{\mathrm{Mg}}\exp(-\lambda^2 R)F(R)$$

$$h_\ell=\alpha_\ell+\beta_\ell\rho_{\mathrm{Mg}}^{2/3}+\gamma_\ell\rho_{\mathrm{Mg}}^{4/3}+\chi_\ell\rho_{\mathrm{Mg}}^2$$

ℓ	α_ℓ	β_ℓ	γ_ℓ	χ_ℓ	LDA equilibrium values
s	0.021 69	−0.253 68	−0.040 17	19.842 15	0.035 16
p	0.398 68	−0.223 03	1.358 34	53.366 24	0.523 22

Hopping terms

$$H_{\ell\ell'\mu}(R)=(a_{\ell\ell'\mu}+b_{\ell\ell'\mu}R+c_{\ell\ell'\mu}R^2)\exp(-g^2_{\ell\ell'\mu}R)F(R)$$

$H_{\ell\ell'\mu}$	$a_{\ell\ell'\mu}$	$b_{\ell\ell'\mu}$	$c_{\ell\ell'\mu}$	$g_{\ell\ell'\mu}$	a	c	$\sqrt{3}a$
$H(ss\sigma)$	5715.097	−310.8836	−182.0526	1.355 79	−0.053 72	−0.024 95	−0.000 09
$H(sp\sigma)$	5704288.	541286.7	−387450.5	1.845 06	−0.012 59	−0.001 61	−0.000 00
$H(pp\sigma)$	−1920.935	498.3775	−22.581 29	1.124 82	0.137 20	0.095 57	0.001 41
$H(pp\pi)$	2000.513	−739.8181	70.265 17	1.131 70	0.044 14	0.038 61	0.002 41

Overlap terms

$$S_{\ell\ell'\mu}(R)=(\delta_{\ell\ell'}+t_{\ell\ell'\mu}R+q_{\ell\ell'\mu}R^2+r_{\ell\ell'\mu}R^3)\exp(-u^2_{\ell\ell'\mu}R)F(R)$$

$S_{\ell\ell'\mu}$	$t_{\ell\ell'\mu}$	$q_{\ell\ell'\mu}$	$r_{\ell\ell'\mu}$	$u_{\ell\ell'\mu}$	a	c	$\sqrt{3}a$
$S(ss\sigma)$	1.048 86	−1.271 81	0.553 82	1.016 29	0.185 12	0.126 83	0.007 67
$S(sp\sigma)$	0.417 81	0.036 30	−0.008 73	0.633 96	0.192 74	0.133 73	−0.008 15
$S(pp\sigma)$	−24.363 68	0.175 41	0.416 61	1.073 40	−0.071 74	−0.018 67	0.001 01
$S(pp\pi)$	-68.959 74	5.975 17	2.558 26	1.193 38	0.080 07	0.047 31	0.000 88

B-B interactions

On-site parameters ($\lambda=0.79205$ a.u.$^{-1/2}$)

$$\rho_{\mathrm{B}}=\Sigma_{\mathrm{B}}\exp(-\lambda^2 R)F(R)$$

$$h_\ell=\alpha_\ell+\beta_\ell\rho_{\mathrm{B}}^{2/3}+\gamma_\ell\rho_{\mathrm{B}}^{4/3}+\chi_\ell\rho_{\mathrm{B}}^2$$

ℓ	α_ℓ	β_ℓ	γ_ℓ	χ_ℓ	LDA equilibrium values
s	−0.165 21	−0.000 22	0.025 79	0.090 88	−0.093 56
p	0.388 02	0.000 60	0.005 66	0.019 18	0.403 83

Hopping terms

$$H_{\ell\ell'\mu}(R)=(a_{\ell\ell'\mu}+b_{\ell\ell'\mu}R+c_{\ell\ell'\mu}R^2)\exp(-g^2_{\ell\ell'\mu}R)F(R)$$

$H_{\ell\ell'\mu}$	$a_{\ell\ell'\mu}$	$b_{\ell\ell'\mu}$	$c_{\ell\ell'\mu}$	$g_{\ell\ell'\mu}$	$a/\sqrt{3}$	a	c	$2a/\sqrt{3}$
$H(ss\sigma)$	−7.315 50	2.092 41	−0.233 79	0.855 73	−0.259 08	−0.044 71	−0.030 32	−0.028 81
$H(sp\sigma)$	−146.6733	64.755 72	−8.573 86	1.219 83	−0.187 43	−0.011 12	−0.005 38	− 0.004 84
$H(pp\sigma)$	−296.2214	128.0942	−10.429 90	1.172 20	0.147 03	0.035 37	0.012 10	0.010 30
$H(pp\pi)$	167.1287	−84.955 81	9.407 29	1.160 57	−0.128 34	−0.004 48	0.002 04	0.002 32

TABLE I. (*Continued*).

Overlap terms

$$S_{\ell\ell'\mu}(R)=(\delta_{\ell\ell'}+t_{\ell\ell'\mu}R+q_{\ell\ell'\mu}R^2+r_{\ell\ell'\mu}R^3)\exp(-u^2_{\ell\ell'\mu}R)F(R)$$

$S_{\ell\ell'\mu}$	$t_{\ell\ell'\mu}$	$q_{\ell\ell'\mu}$	$r_{\ell\ell'\mu}$	$u_{\ell\ell'\mu}$	$a/\sqrt{3}$	a	c	$2a/\sqrt{3}$
$S(ss\sigma)$	0.089 74	−0.058 65	0.004 46	0.601 30	0.245 35	0.053 20	0.030 92	0.028 70
$S(sp\sigma)$	14.028 93	−2.432 93	0.339 14	1.273 02	0.148 23	0.005 81	0.002 08	0.001 81
$S(pp\sigma)$	−60.706 29	−0.475 90	3.294 98	1.321 65	−0.258 33	0.011 41	0.005 58	0.004 97
$S(pp\pi)$	18.987 64	6.133 69	−3.447 42	1.418 89	0.006 89	−0.003 21	−0.001 12	−0.000 96

Mg-B interactions

Hopping terms

$$H_{\ell\ell'\mu}(R)=(a_{\ell\ell'\mu}+b_{\ell\ell'\mu}R+c_{\ell\ell'\mu}R^2)\exp(-g^2_{\ell\ell'\mu}R)F(R)$$

$H_{\ell\ell'\mu}$	$a_{\ell\ell'\mu}$	$b_{\ell\ell'\mu}$	$c_{\ell\ell'\mu}$	$g_{\ell\ell'\mu}$	$\sqrt{\frac{1}{3}a^2+\frac{1}{4}c^2}$	$\sqrt{\frac{4}{3}a^2+\frac{1}{4}c^2}$	$\sqrt{\frac{7}{3}a^2+\frac{1}{4}c^2}$
$H(ss\sigma)$	−15.406 26	8.923 32	−2.258 90	1.062 63	−0.118 87	−0.017 09	−0.002 57
$H(sp\sigma)$	−22.651 45	5.350 89	−0.606 79	1.032 05	−0.076 42	−0.006 12	−0.000 93
$H(pp\sigma)$	98.382 28	−45.014 79	6.057 11	1.208 23	0.022 45	0.001 96	0.000 19
$H(pp\pi)$	−94.472 30	33.606 39	−4.254 18	1.211 06	−0.032 69	−0.001 52	−0.000 13
$H(ps\sigma)$	7.805 80	1.713 00	−0.224 42	1.032 01	0.076 62	0.003 08	0.000 15

Overlap terms

$$S_{\ell\ell'\mu}(R)=(t_{\ell\ell'\mu}+q_{\ell\ell'\mu}R+r_{\ell\ell'\mu}R^2)\exp(-u^2_{\ell\ell'\mu}R)F(R)$$

$S_{\ell\ell'\mu}$	$t_{\ell\ell'\mu}$	$q_{\ell\ell'\mu}$	$r_{\ell\ell'\mu}$	$u_{\ell\ell'\mu}$	$\sqrt{\frac{1}{3}a^2+\frac{1}{4}c^2}$	$\sqrt{\frac{4}{3}a^2+\frac{1}{4}c^2}$	$\sqrt{\frac{7}{3}a^2+\frac{1}{4}c^2}$
$S(ss\sigma)$	1.748 20	0.135 46	0.074 34	0.824 25	0.168 73	0.044 50	0.012 78
$S(sp\sigma)$	15.272 43	3.722 17	0.270 51	1.091 73	0.149 59	0.008 48	0.000 81
$S(pp\sigma)$	−4.517 69	−4.964 27	0.718 42	0.953 39	−0.175 03	−0.002 29	0.001 88
$S(pp\pi)$	846.581 08	265.438 83	−10.035 35	1.306 00	0.061 08	0.001 87	0.000 07
$S(ps\sigma)$	−2.811 56	0.207 00	−0.404 04	0.924 59	−0.198 12	−0.041 68	−0.009 40

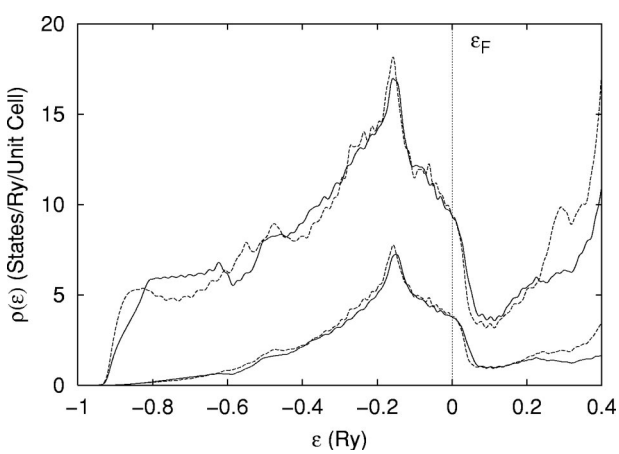

FIG. 2. The electronic density of states (DOS) of MgB_2 in the AlB_2 structure at the theoretical equilibrium volume, comparing the total DOS as determined by the full-potential LAPW method (upper solid line) and our tight-binding parametrization (upper dashed line), and the partial single-atom B p decomposition (lower lines). The LAPW result decomposition was determined inside the muffin tin and then scaled by a factor of 2.37 (see text).

mentum components add up to the total DOS, as is the case in the TB. For the boron states this amounted to multiplying the decomposed values by 2.37. The B s components of the DOS have their strongest presence at the bottom of the valence band, from -0.8 Ry to -0.6 Ry on our scale. They are much smaller than the p-like DOS, so we chose not to include them in Fig. 2. Additionally, we have omitted the Mg p-like DOS, which is also small below ε_F, although it becomes significant above ε_F. Our TB value of the total DOS at ε_F is $N(\varepsilon_F)=0.69$ states/eV, which is almost identical to that found from our direct LAPW calculation. This value of $N(\varepsilon_F)$ corresponds to the LDA equilibrium volume and is slightly smaller than the value of 0.71 states/eV reported by other workers[4–8] at the experimental volume. Using our value of $N(\varepsilon_F)$ and the measured value[3] of the specific-heat coefficient γ we infer a value of $\lambda=0.65$, which is consistent with the high superconducting-transition temperature in MgB_2. It should also be noted that the B p states contribute 81% of the DOS at ε_F.

Our TB Hamiltonian also provides an accurate description of the energetics of MgB_2, which is expected to be very useful for other theoretical studies. We have further tested our parameters by computing the TB equilibrium structure.

We find an equilibrium of $c=6.66$ a.u. and $a=5.79$ a.u., in good agreement with the LAPW result. At $c/a=1.14$ (the experimental value), we deduce a bulk modulus of $B=165$ GPa which is in good agreement with the experimental value of 120 GPa and with the calculated value of 147 GPa reported by Bohnen *et al.*[6]

The TB parameters presented in this paper give a very accurate description of the band structure of MgB_2. The availability of this Hamiltonian should motivate the calculation of other properties of this important material.

We thank I. I. Mazin and D. J. Singh for useful discussions. This work was supported by the U.S. Office of Naval Research. The development of the tight-binding codes was supported in part by the U.S. Department of Defense Common HPC Software Support Initiative (CHSSI).

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] P.C. Canfield, D.K. Finnemore, S.L. Bud'ko, J.E. Ostenson, G. Lapertot, C.E. Cunningham, and C. Petrovic, Phys. Rev. Lett. **86**, 2423 (2001).
[3] Y. Wang, T. Plackowski, and A. Junod, Physica C **355**, 179 (2001).
[4] J.M. An and W.E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
[5] J. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, and L.L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
[6] K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. **86**, 5771 (2001).
[7] Y. Kong, O.V. Dolgov, O. Jepsen, and O.K. Andersen, Phys. Rev. B **64**, 020501 (2001).
[8] A.Y. Liu, I.I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[9] M. Mehl, D. Papaconstantopoulos, and D. Singh, Phys. Rev. B **64**, 140509 (2001).
[10] R.E. Cohen, M.J. Mehl, and D.A. Papaconstantopoulos, Phys. Rev. B **50**, 14 694 (1994).
[11] M.J. Mehl and D.A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996).
[12] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[13] D. Singh, H. Krakauer, and C.S. Wang, Phys. Rev. B **34**, 8391 (1986).
[14] L. Hedin and B.L. Lundqvist, J. Phys. C **4**, 2064 (1971).
[15] N. Bernstein, M.J. Mehl, D.A. Papaconstantopoulos, N.I. Papanicolaou, M.Z. Bazant, and E. Kaxiras, Phys. Rev. B **62**, 4477 (2000).