

# Study of temperature dependent atomic correlations in MgB<sub>2</sub>

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**Abstract.** We have studied temperature evolution of the local as well as the average crystal structure of MgB<sub>2</sub> using real-space atomic pair distribution function (PDF) measured by high resolution neutron powder diffraction in a wide temperature range of  $T = 10$ –600 K. We find small positive correlation factors for the B–B and B–Mg pairs, determined by mean-square displacements (MSD) and the mean-square relative displacements (MSRD). We analyze the PDF using both Einstein and force constant models finding a good agreement between the experimental data and the two models. This indicates that B and Mg atomic correlations are not sensitive to the details of phonon dispersion.

**PACS.** 61.12.-q Neutron diffraction and scattering – 63.20.-e Phonons in crystal lattices – 74.70.Ad Metals; alloys and binary compounds (including A15, MgB<sub>2</sub>, etc.)

## 1 Introduction

MgB<sub>2</sub> is the simplest system to investigate the quantum mechanism of the formation of a superconducting condensate with a critical temperature of  $T_c \simeq 40$  K [1], a factor two higher than in all other known intermetallic superconductors. Recently it has been proposed [2–6] that the enhancement of the critical temperature in MgB<sub>2</sub> is due to an exchange-like interband pairing in a multiband superconductor. There are now experimental evidences [7–11] that the MgB<sub>2</sub> is a first clear case of a high  $T_c$  multiband superconductor, showing two-gaps in the  $\sigma$  and  $\pi$  bands respectively, in agreement with the theory [12,13].

One of the characteristic features of the MgB<sub>2</sub> is that the electron-phonon interaction constructs a weak pairing in the  $\pi$  channel and a strong pairing in the  $\sigma$ -channel. Electronic band structure calculations [14–18], Raman [16,19] and inelastic neutron scattering experiments [20] provide evidence for an extremely large deformation potential for the B bond stretching modes, which gives rise to strongly anharmonic phonons. There is now a general agreement that this strong electron-phonon coupling is mainly driven by the interaction between electronic carriers in the 2D  $\sigma$  band with boron  $p_{x,y}$  character and the zone center  $E_{2g}$  phonon mode [12–17]. This is reflected in a Kohn anomaly in the phonon dispersion related to the size of the small 2D tubular Fermi surfaces

[20]. The proximity of the Fermi level to the Van Hove singularity (VHs) and to the band edge discloses a new scenario where the large amplitude of the expected boron zero point lattice fluctuations [7,12,15,18,21,22] induces large fluctuations of the same order of the separation between the VHs, the gap edge and the Fermi level itself. Although the amplitude of the lattice fluctuations seems thus to be highly relevant for the superconductivity in MgB<sub>2</sub> there is a lack of experimental information on this key point. Furthermore, although the average structure (P6/mmm) of the MgB<sub>2</sub> system has been exhaustively investigated, there is not yet any study on the local structure, since the usual X-ray local probes, as EXAFS, is limited by poor scattering amplitude due to light atoms.

In view of this, here we have employed high resolution neutron diffraction to obtain the pair distribution function (PDF) of the MgB<sub>2</sub>. Using this approach we have investigated the local as well as the average structure of the MgB<sub>2</sub>, namely the mean-square displacements (MSD) and the mean-square relative displacements (MSRD). The comparison of these quantities permits to extract the correlation factors of the boron-boron ( $\rho_{B-B}$ ) and boron-magnesium ( $\rho_{B-Mg}$ ) pair motions, which are found to be  $\sim 0.1$ , that remain nearly constant in a wide temperature range of 0–600 K. We have also compared the experimental data with a force-constant (CF) model for the phonon dispersion. We estimate the phonon frequency renormalization due to the electron-phonon ( $E_{2g}$  modes) interaction yielding a reduction of  $\Delta\rho_{B-B} \sim -0.03$  in the

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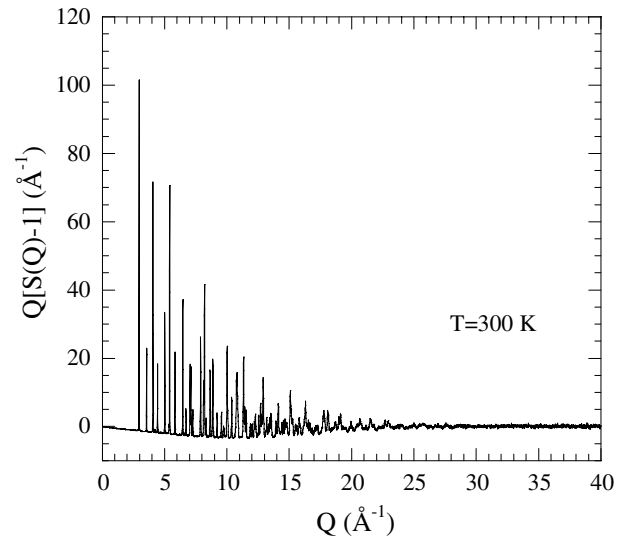
boron-boron correlation factor. While the CF model accounts well the zero temperature values of MSD and the correlated MSRD, the temperature dependence of the MSRD appears to be anomalous. Its physical interpretation provokes new questions on our understanding to the local lattice dynamics in this material.

## 2 Experimental method and data processing

Polycrystalline samples of  $\text{MgB}_2$  were synthesized at high temperature by direct reaction of the elements in a tantalum crucible under argon atmosphere using pure  $^{11}\text{B}$  isotopes. Time-of-flight neutron powder diffraction data were collected on the NPDF diffractometer at the Manuel Lujan, Jr, Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. The NPDF diffractometer, with its high neutron flux and backscattering detector modules provides a high resolution [23], permitting access to a wide range of momentum transfer with sufficient counting statistics making it ideal for PDF studies. The powdered samples were sealed inside extruded cylindrical vanadium containers. These were mounted on the stage of a cryofurnace with and without heat-shield for  $T < 300$  K and  $T > 300$  K, respectively. The scattering data from the empty cryo-furnace, with and without heat-shield, an empty container mounted on the cryofurnace, and the empty instrument were also collected, allowing us to assess and subtract instrumental backgrounds. The scattering from a vanadium rod was also measured to allow the data to be normalized for the incident spectrum and detector efficiencies. We collected each diffraction spectrum up to the high momentum transfer of  $Q = 40 \text{ \AA}^{-1}$  in 3 h. The high resolution diffraction spectrum so obtained presents both the Bragg peaks and the diffuse scattering. While the Bragg peaks reflect the long-range order of the crystalline samples, the oscillating diffuse scattering contains local structural information including the correlated dynamics [24,25]. The PDF is obtained from a Fourier transform of the powder diffraction spectrum (Bragg peaks + diffuse scattering) [26]. It consists of a series of peaks, the positions of which give the distances of atom pairs in the real space, while the ideal width of these peaks is due both to relative thermal atomic motion and to static disorder. This permits the study of the effects of lattice fluctuations on PDF peak widths and yields information on both mean-square displacements and the mean-square relative displacements of atom pairs and their correlations.

Standard data corrections [26] were carried out using the program PDFGETN [27]. After being corrected, the data were normalized by the total scattering cross section of the sample to yield the total scattering structure function  $S(Q)$ . Afterwards, the total scattering structure function  $S(Q)$  is converted to the PDF,  $G(r)$ , by means of a sine Fourier transform according to the relation:

$$\begin{aligned} G(r) &= 4\pi r(\rho(r) - \rho_0) \\ &= \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ. \end{aligned} \quad (1)$$



**Fig. 1.** The reduced structure function  $Q[S(Q) - 1]$  for  $\text{MgB}_2$  measured at 300 K.

We modeled the PDF using a structural model that takes advantage of the definition of the radial distribution function RDF  $R(r)$ , namely:

$$R(r) = rG(r) + 4\pi r^2 \rho_0 = \sum_{i \neq j} \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}), \quad (2)$$

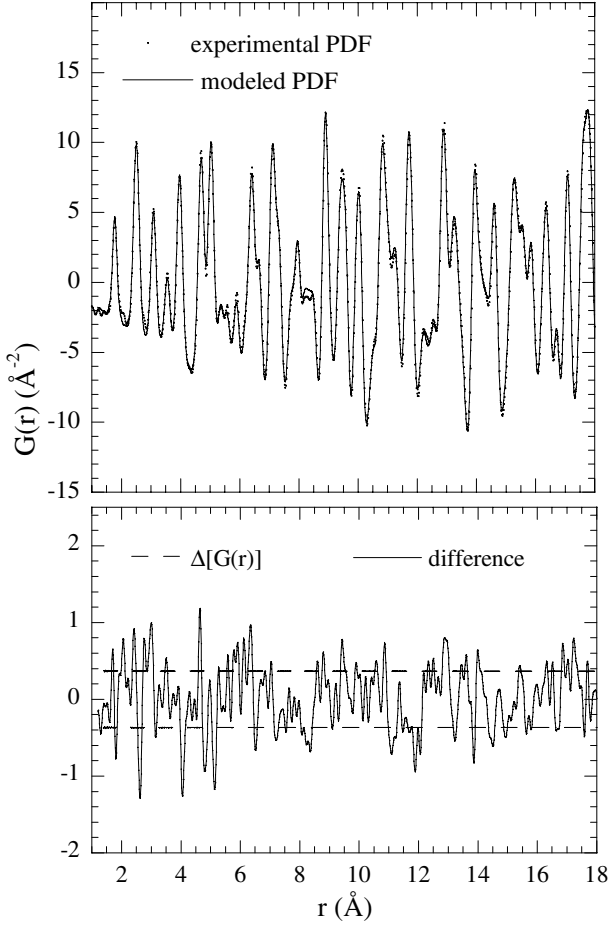
where  $b_i$  is the scattering length of the  $i$ th atom,  $\langle b \rangle$  is the scattering length averaged over the sample composition,  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between the  $i$ th and the  $j$ th atoms, and the sums are taken over all the atoms in the sample. Before being compared to the data, the calculated  $G(r)$  is convoluted with a termination function,  $\sin(Q_{\text{max}}r)/r$  to account for the effects of the finite data collection range. Fundamental lattice information, such as the average crystal structure, the lattice constants, a scale factor, and the refined atomic (thermal) displacement parameters, can now be extracted from the PDF by using the PDF refinement program PDFFIT [28] that is based on a least-squares approach to fit the PDF profile. The mean square displacement of atom  $i$  along the major axes  $x$ ,  $y$ , and  $z$ ,  $\sigma^2(i_x)$ ,  $\sigma^2(i_y)$ ,  $\sigma^2(i_z)$ , are defined as

$$\sigma^2(i_\alpha) = \langle [\mathbf{u}_i \cdot \hat{\mathbf{r}}_\alpha]^2 \rangle, \quad (3)$$

where  $\mathbf{u}_i$  is the lattice displacement of atom  $i$  from its average position [29] and  $\hat{\mathbf{r}}_\alpha$  is the unit vector pointing along the direction  $\alpha = x, y, z$ . Due to the geometry of these compounds, the two boron atoms in the unit cell are equivalent and  $\sigma^2(i_x) = \sigma^2(i_y)$  for all the atoms, so that only four parameters were needed namely  $\sigma^2(\text{B}_{xy})$ ,  $\sigma^2(\text{B}_z)$ ,  $\sigma^2(\text{Mg}_{xy})$  and  $\sigma^2(\text{Mg}_z)$ .

## 3 Results and discussion

In Figure 1 we have shown the reduced scattering structure function  $Q[S(Q) - 1]$  for the  $\text{MgB}_2$  at  $T = 300$  K,

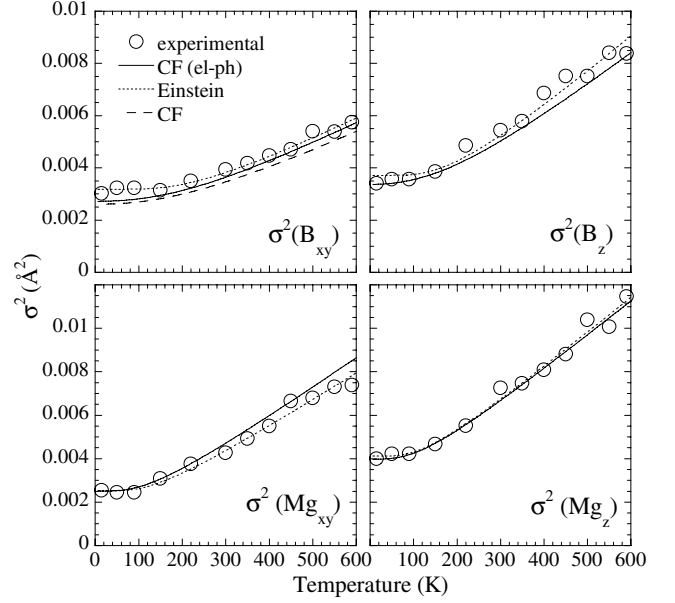


**Fig. 2.** (Upper panel) The PDF  $G(r) = 4\pi r[\rho(r) - \rho_0]$ , obtained from equation (1) for MgB<sub>2</sub>, measured at 300 K (dots), with the structure refinement curve obtained by a least-squares approach (solid line). (Lower panel) The difference curve (solid line) of the experimental PDF with the modeled fit and the standard deviation on the data  $\pm\Delta[G(r)]$  (dashed lines) are shown. We can observe that most of the fluctuations in the difference curve are within  $\pm\Delta[G(r)]$ .

while the corresponding reduced PDF,  $G(r)$ , obtained using equation (1), is shown in Figure 2. The features of the NPDF diffractometer allowed us to obtain high quality PDFs as can be noted by inspecting the modeled fit (solid line) of the  $G(r)$  in the upper panel (Fig. 2). This can be seen also in the lower panel of Figure 2 where most of the fluctuations in the difference curve (solid line) are within the standard deviation of the data  $\pm\Delta[G(r)]$  (dashed lines above and below the difference curve).

The PDF's have been fit over the range 1–18  $\text{\AA}$  using a hexagonal crystal structure (space group P6/mmm), obtaining very good fits at all temperatures. The Bragg peaks are clearly persistent up to 25  $\text{\AA}^{-1}$ , reflecting both the long-range order of the crystalline samples and the small amount of positional (vibrational or static) disorder of the atoms around their average positions.

The lattice parameters at  $T = 300$  K for MgB<sub>2</sub> ( $T_c \sim 39$  K) were found to be  $a = 3.08505(4)$   $\text{\AA}$ ,  $c = 3.5218(1)$   $\text{\AA}$ . The mean square displacements  $\sigma^2(B_{xy})$ ,



**Fig. 3.** Anisotropic in plane  $\sigma^2(B_{xy})$ ,  $\sigma^2(Mg_{xy})$  and along the  $c$ -axis  $\sigma^2(B_z)$ ,  $\sigma^2(Mg_z)$  mean-square displacements for the B and Mg atoms, as a function of the temperature. The open circles represent the PDFFIT refined values, while the solid and the dotted lines represent the modeled data in the CF and Einstein model, respectively. The errorbars in the  $\sigma^2(i_\alpha)$  are smaller than the size of the used symbols (open circles). The dashed line shows the in-plane boron displacements in the CF model in the absence of the electron-phonon interaction.

$\sigma^2(B_z)$ ,  $\sigma^2(Mg_{xy})$ ,  $\sigma^2(Mg_z)$  are shown in Figure 3 (open circles).

### 3.1 Atomic mean-square displacements

In order to extract information about the phonon spectrum, we fit each MSD with a simple Einstein model,

$$\sigma^2(i_\alpha) = \frac{\hbar}{M_i \omega_{i_\alpha}} \left[ \frac{1}{2} + n[\omega(i_\alpha)] \right] + \sigma_0^2(i_\alpha), \quad (4)$$

where  $\sigma_0^2(i_\alpha)$  takes into account the static disorder,  $M_i$  is atomic mass of the atom  $i$  and  $\omega(i_\alpha)$  provided an estimate of the vibrational frequency of the atom  $i$  along the direction  $\alpha$ . The quantity  $n(x)$  is the Bose thermal factor  $n[x] = [\exp(x/k_B T) - 1]^{-1}$ . The values of the fitting parameters,  $\omega_{i_\alpha}$  and  $\sigma_0^2(i_\alpha)$ , are reported in Table 1, and the  $\sigma^2$  vs.  $T$  fitting curves are represented by dotted lines in Figure 3. The different values of  $\omega_{i_\alpha}$  represent the different energy range of the phonon spectra associated with the boron and magnesium in-plane and out-of-plane lattice vibrations, and they are in good agreement with the corresponding spectra reported in reference [30].

As shown we find that, apart from small static disorder in  $\sigma_0^2(Mg_z)$ , a simple Einstein model seems to describe quite well the lattice vibrations in this compound. Moreover, the Einstein fits were obtained by simply using nominal atomic masses  $M_{Mg} = 24.3$  a.m.u. for  $\sigma^2(Mg)$

**Table 1.** “Effective” phonon frequencies  $\omega_{i_\alpha}$  and static disorder contributions  $\sigma_0^2(i_\alpha)$  for the in-plane and out-of-plane B and Mg displacements as obtained by the Einstein model fit [Eq. (4)] of  $\sigma^2(i_\alpha)$ .

$\omega(\text{B}_{xy})$ (K)	$703 \pm 10$
$\omega(\text{B}_z)$ (K)	$572 \pm 15$
$\omega(\text{Mg}_{xy})$ (K)	$398 \pm 6$
$\omega(\text{Mg}_z)$ (K)	$350 \pm 9$
$\sigma_0^2(\text{B}_{xy})$ ( $\text{\AA}^2$ )	$\leq 5 \times 10^{-5}$
$\sigma_0^2(\text{B}_z)$ ( $\text{\AA}^2$ )	$\leq 9 \times 10^{-5}$
$\sigma_0^2(\text{Mg}_{xy})$ ( $\text{\AA}^2$ )	$\leq 7 \times 10^{-5}$
$\sigma_0^2(\text{Mg}_z)$ ( $\text{\AA}^2$ )	$0.0013 \pm 0.0003$

and  $M_B = 10.81$  a.m.u. for  $\sigma^2(\text{B})$ . This means that we are implicitly assuming the magnesium and boron vibrations being decoupled. The two-parameter fits reproduce the data very well for each of the motions considered. We will be back to discuss this point later.

To gain further insight to this issue we introduce a force-constant (CF) model for the dynamical matrix. We neglect for the moment the effects of the electron-phonon interaction, which leads to renormalized phonon frequencies and anharmonicity, and we assume the lattice dynamics to be harmonic. This will enable us to evaluate eigenvectors  $\hat{\epsilon}_{\mathbf{q},\mu}$  and eigenvalues  $\omega_{\mathbf{q},\mu}$  of the lattice modes for each point of the phonon Brillouin zone. The phonon contribution to the lattice displacements  $\sigma^2(i_\alpha)$  [ $\sigma^2(i_\alpha) = \sigma_{\text{ph}}^2(i_\alpha) + \sigma_0^2(i_\alpha)$ ] will thus be obtained as [31]:

$$\sigma_{\text{ph}}^2(i_\alpha) = \frac{\hbar}{N} \sum_{\mathbf{q},\mu} \frac{|\epsilon_{\mathbf{q},\mu}^{i_\alpha}|^2}{M_i \omega_{\mathbf{q},\mu}} \left[ \frac{1}{2} + n(\omega_{\mathbf{q},\mu}) \right], \quad (5)$$

where  $\epsilon_{\mathbf{q},\mu}^{i_\alpha}$  is the component of the eigenvector  $\hat{\epsilon}_{\mathbf{q},\mu}$  concerning to the displacement of the  $i$  atom along the  $\alpha$  direction and  $N$  is the total number of  $\mathbf{q}$ -points considered in the phonon Brillouin zone. From a general point of view, since  $\sigma_{\text{ph}}^2(i_\alpha)$  involves an integral over the whole Brillouin zone and over all the phonon branches, it will not be sensitive to the fine details of the phonon dispersion but only to its gross features. For this reason, and in order to preserve the simplicity of our analysis, we limit ourselves to consider only four elastic springs,  $\phi$ ,  $\chi$ ,  $\kappa$  and  $\psi$ , connecting, respectively, in-plane B–B nearest neighbors, out of plane B–B nearest neighbors, out-of-plane B–Mg nearest neighbors, and in-plane Mg–Mg nearest neighbors. Each elastic spring is specified by its tensor components (ex.:  $\phi_r$ ,  $\phi_{\parallel}$ ,  $\phi_{\perp}$ ), corresponding respectively to the lattice displacements along the radial (bond-stretching) direction and along the in-plane and out-of-plane tangential (bond-bending) directions. In  $\text{MgB}_2$  we choose the constants  $\phi_r$ ,  $\phi_{\parallel}$ ,  $\phi_{\perp}$ ,  $\chi_r$ ,  $\chi_{\parallel}$ ,  $\chi_{\perp}$ ,  $\kappa_r$ ,  $\kappa_{\parallel}$ ,  $\kappa_{\perp}$ ,  $\psi_r$ ,  $\psi_{\parallel}$ ,  $\psi_{\perp}$ , to fit the local-density functional (LDA) phonon dispersion of reference [16] along the high-symmetry points of the Brillouin zone. Since the force-constant model is meant to reproduce the bare phonon dispersion, in the present analysis we deliberately did not include the  $E_{2g}$  phonon frequencies

**Table 2.** Force-constant parameters reproducing the bare phonon dispersion in  $\text{MgB}_2$  in the absence of electron-phonon interaction.

$\phi_r$ (eV/ $\text{\AA}^2$ )	$\phi_{\parallel}$ (eV/ $\text{\AA}^2$ )	$\phi_{\perp}$ (eV/ $\text{\AA}^2$ )
12,45	49.80	21.17
$\chi_r$ (eV/ $\text{\AA}^2$ )	$\chi_{\parallel}$ (eV/ $\text{\AA}^2$ )	$\chi_{\perp}$ (eV/ $\text{\AA}^2$ )
0.0	16.6	0.0
$\kappa_r$ (eV/ $\text{\AA}^2$ )	$\kappa_{\parallel}$ (eV/ $\text{\AA}^2$ )	$\kappa_{\perp}$ (eV/ $\text{\AA}^2$ )
0.84	1.50	9.14
$\psi_r$ (eV/ $\text{\AA}^2$ )	$\psi_{\parallel}$ (eV/ $\text{\AA}^2$ )	$\psi_{\perp}$ (eV/ $\text{\AA}^2$ )
0.0	9.34	0.42

at the zone centers  $\Gamma$ ,  $A$ , which are known to be strongly affected by the el-ph interaction. The force constants obtained from this fitting procedure are reported in Table 2.

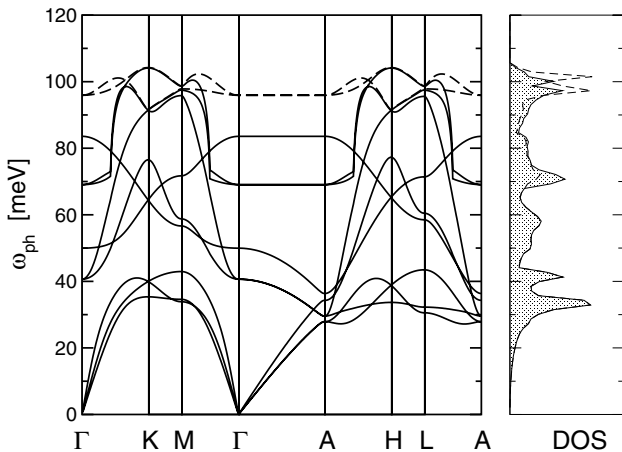
As mentioned in the introduction, the  $E_{2g}$  phonon modes close to the  $\Gamma$  and  $A$  points are expected to be strongly affected by the interaction with the almost 2D parabolic  $\sigma$  bands, giving rise to a remarkable softening of the  $E_{2g}$  phonon frequencies for  $|\mathbf{q}| \leq 2k_F$ , where  $k_F$  is the Fermi vector of the  $\sigma$  bands [14–17, 20, 32]. We include these effects through the self-energy renormalization of the phonon frequencies:

$$\Omega_{E_{2g}}^2(\mathbf{q}) = \omega_{E_{2g}}^2(\mathbf{q}) - (4N_\sigma g^2 f_{\text{anharm}}/M_B) \Pi_{2D}(\mathbf{q}),$$

where  $N_\sigma$  is density of states of the  $\sigma$  bands per spin and per band,  $g$  the electron-phonon matrix element between  $\sigma$ -band electrons and the  $E_{2g}$  phonon mode at the zone center and  $f_{\text{anharm}}$  is a dimensionless factor accounting for the anharmonic hardening of the  $E_{2g}$  phonon modes due to the electron-phonon coupling itself. Moreover the factor 4 takes into account the spin and band degeneracy and  $\Pi_{2D}(\mathbf{q})$  is the two-dimensional Lindhardt function  $\Pi_{2D}(x) = \theta(1-x) + \theta(x-1)[x - \sqrt{x^2-1}]/x^4$ , with  $x = |\mathbf{q}|/2k_F$ . We take, from first-principle calculations [14, 15, 18],  $f_{\text{anharm}} = 1.25$ ,  $N_\sigma = 0.075$  states/(eV spin cell)  $g = 12$  eV/ $\text{\AA}$  [14, 15, 18], and  $k_F \simeq \pi/12d_{\text{B-B}}$ , where  $d_{\text{B-B}}$  is the boron-boron distance.

The phonon dispersion and phonon density of states (PDOS) of the force-constant model are shown in Figure 4, that are in good agreement with the LDA calculations of reference [16]. For comparison, the dashed lines represent the bare phonon dispersion in the absence of el-ph interaction and the corresponding PDOS. Most striking is a partial shift in spectral weight from 100 meV to 70 meV when the el-ph coupling is turned on, due to the softening of the flat  $\Gamma - A$  band originating from the  $E_{2g}$  phonons.

The lattice displacements for each atom and for each direction can now be evaluated directly by means of equation (5). The results are also shown in Figure 3 along with the data extracted by the PDF analysis and with the simple Einstein fits. In spite of the crude simplification of the phonon dispersion, the agreement with the PDF data is remarkable. Just as in the Einstein fits, we find that a constant shift  $\sigma_0^2(\text{Mg}_z) \simeq 0.0013 \text{ \AA}^2$  due to intrinsic disorder is needed to account for the magnesium out-of-plane lattice vibration



**Fig. 4.** Phonon dispersion and phonon density of states for MgB<sub>2</sub> evaluated within the CF model. Dashed lines represent the same quantities without taking into account the electron-phonon interaction.

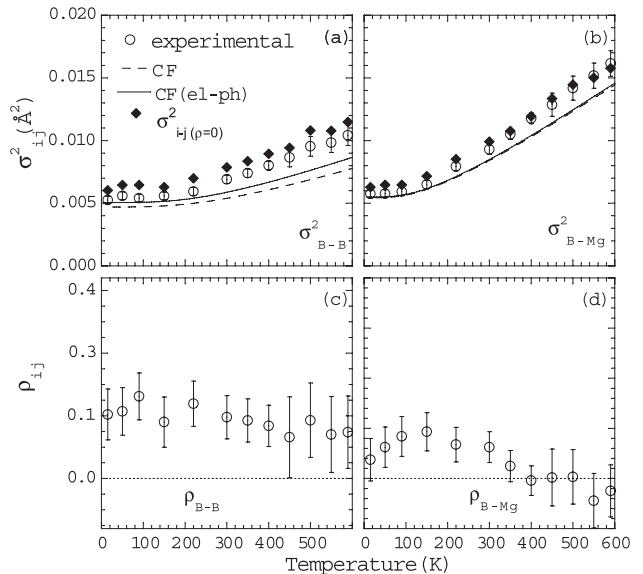
while the contribution of the disorder for the other modes is found to be negligible. Note that the agreement between the data and solid lines was obtained with *no adjustable parameters*. The values used in the force-constant models in Table 2 were indeed fit to reproduce the theoretical LDA calculation and not the PDF data and the only other parameter, the static disorder parameter in  $\sigma_0^2(\text{Mg}_z)$ , was the same value as was used in the Einstein fits.

To point out the explicit role of the electron-phonon interaction, we show also in the left-upper panel of Figure 3 the  $\sigma_0^2(\text{B}_{xy})$  lattice displacements in the absence of the el-ph frequency renormalization. Since only  $E_{2g}$  phonons are coupled, only the  $\sigma_0^2(\text{B}_{xy})$  lattice displacements result modified. We note that the inclusion of electron-phonon interaction effects leads to a slight increase of the amount of the boron in-plane lattice displacements, with a better agreement with the experimental data. The increase of  $\sigma_0^2(\text{B}_{xy})$  is easily understandable as due to the softening of the  $E_{2g}$  phonon mode. On the other hand, since the electron-phonon renormalization effects are restricted to a small region  $\sqrt{q_x^2 + q_y^2} \leq 2k_F$  of the whole Brillouin zone, the impact of the el-ph coupling on the total amount of the lattice displacements  $\sigma_0^2(\text{B}_{xy})$  is relatively weak.

### 3.2 Correlations in the B–B and B–Mg atomic pairs motion

Above we have shown that the MSD in the MgB<sub>2</sub> (Debye-Waller factor in crystallography) are well explained by harmonic models with independent boron and magnesium motions. The PDF technique is sensitive to the correlations in the atomic dynamics that contain some additional details about the underlying interatomic potentials [24, 25, 29, 33, 34]. Here we explore the motional correlations in the MgB<sub>2</sub> using the PDF data.

The Gaussian width  $\sigma_{ij}$  of the PDF peaks is directly related to the mean-square relative displacement (MSRD)



**Fig. 5.** Mean-square relative lattice displacements  $\sigma_{\text{B-B}}^2$  (a),  $\sigma_{\text{B-Mg}}^2$  (b), as extracted from the width of the PDF peaks and the corresponding correlation function  $\rho_{\text{B-B}}$  (c),  $\rho_{\text{B-Mg}}$  (d) (open circles). Same quantities evaluated within the CF model with and without the electron-phonon interaction are shown respectively by solid and dashed lines respectively. The filled diamonds represent lattice displacements  $\sigma_{\text{B-B}}^2$ ,  $\sigma_{\text{B-Mg}}^2$  for completely uncorrelated lattice motion, i.e.  $\rho_{ij} = 0$ .

of atomic pairs projected onto the vector joining the atom pairs [29], i.e.

$$\sigma_{ij}^2 = \langle [(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 \rangle, \quad (6)$$

where  $\mathbf{u}_i$  and  $\mathbf{u}_j$  are the lattice displacements of atoms  $i$  and  $j$  from their average positions,  $\hat{\mathbf{r}}_{ij}$  is the unit vector connecting atoms  $i$  and  $j$ , and the angular brackets indicate an ensemble average [29].

In our analysis, we focus on the width of the nearest neighbor boron-boron PDF peak, ( $\sigma_{\text{B-B}}^2$ ), and on the nearest neighbor magnesium-boron peak, ( $\sigma_{\text{B-Mg}}^2$ ). These are well resolved single-component peaks in the PDF whose width directly yields correlated dynamical information [25]. The Gaussian widths  $\sigma_{\text{B-B}}^2$ ,  $\sigma_{\text{B-Mg}}^2$ , as measured by the PDF data are shown in the upper panels of Figure 5 (open circles) along with the same quantity evaluated within the CF model (solid line) according to the relation:

$$\sigma_{ij}^2 = \frac{\hbar}{N} \sum_{\mathbf{q}, \mu} \left[ \frac{1}{2} + n(\omega_{\mathbf{q}, \mu}) \right] \left\{ \frac{|\hat{\epsilon}_{\mathbf{q}, \mu}^i \cdot \hat{\mathbf{r}}_{ij}|^2}{M_i \omega_{\mathbf{q}, \mu}} + \frac{|\hat{\epsilon}_{\mathbf{q}, \mu}^j \cdot \hat{\mathbf{r}}_{ij}|^2}{M_j \omega_{\mathbf{q}, \mu}} - \frac{2\text{Re} \left[ (\hat{\epsilon}_{\mathbf{q}, \mu}^i \cdot \hat{\mathbf{r}}_{ij})(\hat{\epsilon}_{\mathbf{q}, \mu}^{j*} \cdot \hat{\mathbf{r}}_{ij}) e^{i\mathbf{q} \cdot \mathbf{r}_{ij}} \right]}{\omega_{\mathbf{q}, \mu} \sqrt{M_i M_j}} \right\}. \quad (7)$$

In the latter case in the right panel for  $\sigma_{\text{B-Mg}}^2$  we have also added a small contribution of the local lattice displacements due to the disorder (see below for more details).

The temperature dependence of the single-atom motions was well explained by the model, but not those of the

correlated  $\sigma_{ij}^2$ , which suggests that the model is not capturing some aspect of the motional correlations. The introduction of the electron-phonon coupling into the model improves the agreement slightly, with a larger effect observed on  $\sigma_{B-B}^2$ , but this does not explain all of the discrepancy. In each case, the pair correlation peaks broaden more quickly in the data than in the model.

As a general consideration, we would like to stress once more that while  $\sigma^2(i_\alpha)$  probes the absolute magnitude of the single atom mean-square displacement,  $\sigma_{ij}^2$  provides information about the *correlation* between the lattice displacements of atom pairs. Let us consider for instance the case of  $\sigma_{B-B}^2$  which involves only boron in-plane lattice fluctuations. We can identify three limiting behaviors for this quantity: (i) perfectly in-phase lattice motion; (ii) perfectly opposite-phase motion; (iii) completely independent motion. In the first case it is easy to see that  $\sigma_{B-B}^2 = 0$ , while  $\sigma_{B-B}^2 = 2\sigma^2(B_{xy})$  when the nearest neighbor boron lattice displacements are uncorrelated, and  $\sigma_{B-B}^2 = 4\sigma^2(B_{xy})$  when they have opposite phase.

To formalize this we rearrange equation (6) as

$$\sigma_{ij}^2 = \langle [(\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij})^2] \rangle + \langle [(\mathbf{u}_j \cdot \hat{\mathbf{r}}_{ij})^2] \rangle - 2\langle (\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij}) \cdot (\mathbf{u}_j \cdot \hat{\mathbf{r}}_{ij}) \rangle. \quad (8)$$

Here the first two terms are related to mean-square thermal displacement of atoms  $i$  and  $j$  projected along  $\hat{\mathbf{r}}_{ij}$ , while the third term is a displacement correlation function, which carries information about the motional correlations. It is now useful to quantify the degree of correlation by introducing the dimensionless correlation parameter  $\rho_{ij}$  defined as [24, 25, 33, 35]:

$$\sigma_{ij}^2 = \sigma^2(i_j) + \sigma^2(j_i) - 2\sigma(i_j)\sigma(j_i)\rho_{ij}, \quad (9)$$

where  $\sigma^2(i_j) = \langle [(\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij})^2] \rangle$ . Positive values of  $\rho > 0$  describe a situation where the atoms move in phase, so that the resulting value of  $\sigma_{ij}^2$  is smaller than for the uncorrelated case. On the other hand, a predominance of opposite phase atomic vibrations should result in  $\rho < 0$  and in a PDF peak width  $\sigma_{ij}^2$  larger than the uncorrelated case.

It is important to note that the correlation function  $\rho_{ij}$  in equation (9) expresses the degree of correlation between the *total* atomic displacements. Using equation (9) the correlation parameter can be calculated from the total width of the PDF peak as:

$$\rho_{ij} = \frac{\sigma^2(i_j) + \sigma^2(j_i) - \sigma_{ij}^2}{2\sigma(i_j)\sigma(j_i)}. \quad (10)$$

The phonon correlation factor  $\rho_{ij}$  as extracted from the PDF data  $\sigma_{B-B}^2$ ,  $\sigma_{B-Mg}^2$ , and from the single atom mean-square lattice displacements  $\sigma^2(i_\alpha)$  is shown in the lower panels of Figure 5 (open circles). We find a positive correlation factor for both  $\rho_{B-B} \sim 0.1$  and  $\rho_{B-Mg} \sim 0.1$ , indicating a slight predominance of the in-phase B-B and B-Mg lattice displacements in this experimental probe. Positive values of  $\rho_{ij}$  are commonly reported in a variety of materials. The intuitive explanation is that the in-phase phonon modes (acoustic, low optical branch modes) are

generally less stiff than the opposite-phase optical ones. Our reported values of  $\rho_{B-B}, \rho_{B-Mg} \sim 0.1$  are however much smaller than the correlation factors commonly found in other covalently bonded materials [24, 25, 33, 35].

## 4 Concluding remarks

In this work we have investigated local lattice properties of the MgB<sub>2</sub> paying special attention on the lattice dynamics and the correlations in the B-B and B-Mg first neighbor atomic pair motion. We have used the real space PDF obtained from high resolution neutron diffraction to study the effects of the lattice vibrations on the PDF peak widths. The PDF peaks in well ordered crystals such as the present case yield important information about the underlying atomic potentials through the correlated local lattice dynamics. The data have been modeled using both a multi-parameter force-constant model and a simple Einstein model. We have found that the two models reproduce the average features of the lattice vibrations. The analysis of the PDF peak linewidths permits to evaluate the correlation for both the nearest neighbor B-B and B-Mg atomic pairs. We find a small positive correlation factor  $\rho_{B-B} \sim 0.1$  and  $\rho_{B-Mg} \sim 0.1$ , nearly temperature independent, indicating a weakly prevalent in-phase relative atomic motion.

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