Study of temperature dependent atomic correlations in MgB$_2$

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Abstract. We have studied the evolution with temperature of the local as well as the average crystal structure of MgB$_2$ using the real-space atomic pair distribution function (PDF) measured by high resolution neutron powder diffraction. We have investigated the correlations of the B-B and B-Mg nearest neighbor pair motion by comparing, in the wide temperature range from $T = 10$ K up to $T = 600$ K, the mean-square displacements (MSD) of single atoms with the mean-square relative displacements (MSRD) obtained from the PDF peak linewidths. The results show that the single atom B and Mg vibrations are mostly decoupled from each other, with a small predominance of positive (in phase) correlation factor for both the B-B and B-Mg pairs. The small positive correlation is almost temperature independent, in contrast with our theoretical calculations; this can be a direct consequence of the strong decay processes of the $E_{2g}$ anharmonic phonons.

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1 Introduction

MgB$_2$ is the simplest system to investigate the quantum mechanism that allows the formation of a superconducting condensate with critical temperature $T_c \approx 40$ K [1] a factor two higher than in all other known intermetallic superconductors. It was recently proposed by a few groups [2,3,5,6] that the enhancement of the critical temperature in MgB$_2$ is due to the exchange-like interband pairing in a multiband superconductor. There is now experimental evidence [7,9,10,11] that MgB$_2$ is the 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]

The characteristic feature of MgB$_2$ is that the electron-phonon interaction gives a weak pairing in the $\pi$ channel and a strong pairing in the $\sigma$-channel. Electronic band calculations, [14,15,16,17,18] Raman [16,19] and inelastic neutron scattering experiments [20] provide evidence of an extremely large deformation potential for the B bond stretching modes, which gives rise to strongly anharmonic phonons. This anharmonicity also results in a structural instability (phonon softening) that affects the dynamics of the lattice fluctuations and the local structural properties of the material, as we discuss below. 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. [12,13,14,15,16,17]

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$_2$ there is a lack of experimental information on this key point. Furthermore, although the average structure (P6/mmm) of the MgB$_2$ system has been exhaustively investigated, there is not yet any study of the local structure, since typical x-ray local probes, such as EXAFS, cannot be used to study local structure near light atoms.

In view of this, here we employ high resolution neutron diffraction to obtain the pair distribution function (PDF) of MgB$_2$. In this way we investigate the local as well as the average structure of MgB$_2$, namely the mean-square displacements (MSD) of single atoms and the mean-square relative displacements (MSRD). The comparison of these
quantities permits for the first time to extract the correlation factors $\rho_{\text{B-B}}$, $\rho_{\text{B-Mg}}$, defined below, of the boron-boron and boron-magnesium pair motions, which are found to be $\rho_{\text{B-B}} \sim 0.1$, $\rho_{\text{B-Mg}} \sim 0.1$, and nearly constant in a wide range of temperature $0 \, K < T < 600 \, K$. We also compare the experimental data with a constant force (CF) model for the phonon dispersion. We estimate that the phonon frequency renormalization due to the electron-phonon interaction on the $E_{2g}$ modes yields a reduction $\Delta \rho_{\text{B-B}} \sim -0.03$ in the boron-boron correlation factor. While the CF model can nicely account for the zero temperature values of the single atoms MSD and the correlated MSRD, the temperature behavior of the correlation factor is shown to be highly anomalous and its physical interpretation gives rise to new questions about our understanding to the local lattice dynamics in this material.

2 Experimental method and data processing

Polycrystalline samples of MgB$_2$ were synthesized at high temperature by direct reaction of the elements in a tantalum crucible under argon atmosphere using pure $^{11}$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 has a high resolution, providing access to a broad range of temperature 0 K $< T < 300$ K, respectively. The scattering data from the empty cryofurnace, with and without heat-shield, are equivalent and nearly constant $\Delta \rho$, defined below, of the boron- and boron-magnesium pair motions, which are found in a wide range of temperature $0 \, K < T < 600 \, K$. We also compare the experimental data with a constant force (CF) model for the phonon dispersion. We estimate that the phonon frequency renormalization due to the electron-phonon interaction on the $E_{2g}$ modes yields a reduction $\Delta \rho_{\text{B-B}} \sim -0.03$ in the boron-boron correlation factor. While the CF model can nicely account for the zero temperature values of the single atoms MSD and the correlated MSRD, the temperature behavior of the correlation factor is shown to be highly anomalous and its physical interpretation gives rise to new questions about our understanding to the local lattice dynamics in this material.

Standard data corrections were carried out using the program PDFGETN. 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:

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

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

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

where $b_i$ is the scattering length of the $i^{th}$ atom, $b$ is the scattering length averaged over the sample composition, $r_{ij} = |r_i - r_j|$ 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 that is based on a least-squares approach to fit the PDF profile. The average atomic displacement distribution 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

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

where $\mathbf{u}_i$ is the lattice displacement of atom $i$ from its average position $\mathbf{r}_i$ and $\hat{r}_\alpha$ is the unit vector pointing along the direction $\alpha = x, y, z$. Due to the geometry of these compounds, the two boron atoms for 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 $\sigma^2(B_{xy})$, $\sigma^2(B_z)$, $\sigma^2(Mg_{xy})$ and $\sigma^2(Mg_z)$.

3 Results and discussion

In Fig. we show the reduced scattering structure function $Q[S(Q) - 1]$ for the MgB$_2$ at $T = 300$ K, while the corresponding reduced PDF, $G(r)$, obtained using Eq. (1), is shown in Fig. 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. This can be seen also in the lower panel of Fig. where most of the fluctuations in the difference curve (solid line) are within the standard deviation on the data $\pm \Delta G(r)$ (dashed lines above and below the difference curve).
of the atoms around their average positions.
small amount of positional (vibrational or static) disorder
the long-range order of the crystalline samples and the
peaks are clearly persistent up to 25˚
excellent fits were obtained at all temperatures. The Bragg
hexagonal crystal structure (space group P6/mmm), and
39 K) were found to be
a

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3.1 Atomic mean-square displacements
In order to extract information about the phonon spec-
tum, we fit each lattice displacement with a simple Ein-
stein model,

where \( \sigma^2(i) \) takes into account the static disorder, \( M_i \)
is atomic mass of the atom \( i \) and \( \omega(i) \) provided an es-
imate of the vibrational frequency of the atom \( i \) along
the direction \( \alpha \). The quantity \( n(x) \) is the Bose thermal
factor \( n(x) = [\exp(x/kBT) − 1]^{-1} \). The values of the fit-
ting parameters, \( \omega(i) \) and \( \sigma^2(i) \), are reported in Tab. 1
and the \( \sigma^2 \) vs. \( T \) fitting curves are represented by dotted
lines in Fig. 3. The different values of \( \omega(i) \) 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 Ref. [28].

Quite surprising, we find that, apart from some amount
of disorder in \( \sigma^2_0(Mg_z) \), this simple four-peak Einstein
model seems to describe quite well the lattice vibrations
in this compound. This is quite intriguing because phonon
frequency dispersions are expected to be notably differ-
ent from dispersionless Einstein models in these materials.
Moreover, the Einstein fits were obtained by simply using
an effective atomic mass \( M_{Mg} = 24.3 \) a.m.u. for \( \sigma^2(Mg) \)
and \( M_B = 10.81 \) a.m.u. for \( \sigma^2(B) \). This means that we
are implicitly assuming that magnesium and boron vibra-
tions are totally decoupled from each other. These two-
parameter fits reproduce the data very well for each of
the motions considered. Non-independent boron and mag-
nesium vibrations would lead to deviations from Einstein
behavior that are not evident in the data suggesting that
this approximation is reasonable in this system. We return
to this point below.

To gain further insight on this issue we introduce a
constant force (CF) shell 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

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Fig. 1. The reduced structure function \( Q[S(Q) − 1] \) for MgB₂
measured at 300 K.

The PDF’s have been fit over the range 1–18 Å using a
hexagonal crystal structure (space group P6/mmm), and
excellent fits were obtained at all temperatures. The Bragg
peaks are clearly persistent up to 25 Å⁻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 MgB₂ \( (T_c \sim
39 \) K) were found to be \( a = 3.08505(4) \) Å, \( c = 3.5218(1) \) Å.
The lattice displacements \( \sigma^2(B_{xy}), \sigma^2(B_z), \sigma^2(Mg_{xy}), \sigma^2(Mg_z) \)
are shown in Fig. 3 (open circles).

Fig. 2. (Upper panel) The PDF \( G(r) = 4\pi r [\rho(r) − \rho_0] \),
obtained from Eq. 11 for MgB₂, 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 ± \( \Delta[G(r)] \) (dashed lines) are
shown. We can observe that most of the fluctuations in the
difference curve are within ± \( \Delta[G(r)] \).
dynamics to be harmonic (we shall discuss later and more specifically the role of the electron-phonon interaction and possible effects of the anharmonicity of the $E_{2g}$ phonon mode). This will enable us to evaluate eigenvectors $\xi_{q,\mu}$ and eigenvalues $\omega_{q,\mu}$ of the lattice modes for each point of the phonon Brillouin zone. The phonon contribution to the lattice displacements $\sigma^2(i_\alpha) = \sigma^2_{ph}(i_\alpha) + \sigma^2_0(i_\alpha)$ will be thus obtained as:  

$$
\sigma^2_{ph}(i_\alpha) = \frac{\hbar}{N} \sum_{q,\mu} \left| \xi_{q,\mu}^\alpha \right|^2 \frac{1}{2} + n(\omega_{q,\mu}), 
$$

where $\xi_{q,\mu}^\alpha$ is the component of the eigenvector $\xi_{q,\mu}$ concerning to the displacement of the $i$ atom along the $\alpha$ direction and $N$ is the total number of $q$-points considered in the phonon Brillouin zone. From a general point of view, since $\sigma^2_{ph}(i_\alpha)$ 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.: $\phi$, $\phi||$, $\phi_\perp$, $\chi||$, $\chi_\perp$, $\kappa||$, $\kappa_\perp$, $\psi||$, $\psi_\perp$, $\psi_{\pm 1}$), to fit the local-density functional (LDA) phonon dispersion of Ref. 10 along the high-symmetry points of the Brillouin zone. Since the constant force model is meant to reproduce the bare phonon dispersion, we deliberately did not include in the fit procedure the $E_{2g}$ phonon frequencies at the zone center $\Gamma$, $A$, which are known to be strongly affected by the el-ph interaction. The elastic 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 $|q| \leq 2k_F$, where $k_F$ is the Fermi vector of the $\sigma$ bands.\textsuperscript{14,15,16,17,20} We include these effects through the self-energy renormalization of the phonon frequencies $\Omega_{E_{2g}}(q) = \omega_{E_{2g}}^2(q) - (4N_\sigma g^2 f_{anharm}/M_\beta) \Pi_{2D}(q)$, 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 $f_{anharm}$ 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 $\Pi_{2D}(q)$ is the two-dimensional Lindhardt function $\Pi_{2D}(x) = \theta(1-x) + \theta(x-1)[x - \sqrt{x^2 - 1}] / x^4$, with $x = |q|/2k_F$. We take, from first-principle calculations,\textsuperscript{14,15,18} $f_{anharm} = 1.25$, $N_\sigma = 0.075$ states/(eV \cdot spin \cdot cell) $g = 12$.

### Table 1

| $\omega(B_{2g})$ (K) | $703 \pm 10$ |
| $\omega(B_{2g})$ (K) | $572 \pm 15$ |
| $\omega(Mg_{2g})$ (K) | $398 \pm 6$ |
| $\omega(Mg_{2g})$ (K) | $350 \pm 9$ |
| $\sigma^2_0(B_{2g})$ (Å$^2$) | $\leq 5 \cdot 10^{-9}$ |
| $\sigma^2_0(B_{2g})$ (Å$^2$) | $\leq 6 \cdot 10^{-9}$ |
| $\sigma^2_0(Mg_{2g})$ (Å$^2$) | $\leq 7 \cdot 10^{-9}$ |
| $\sigma^2_0(Mg_{2g})$ (Å$^2$) | $0.0013 \pm 0.0003$ |

### Table 2

| $\phi_r$ (eV/Å$^2$) | $12.45$ |
| $\phi_{||}$ (eV/Å$^2$) | $49.80$ |
| $\phi_\perp$ (eV/Å$^2$) | $21.17$ |
| $\chi_r$ (eV/Å$^2$) | $0.00$ |
| $\chi_{||}$ (eV/Å$^2$) | $16.6$ |
| $\chi_\perp$ (eV/Å$^2$) | $0.0$ |
| $\kappa_r$ (eV/Å$^2$) | $0.84$ |
| $\kappa_{||}$ (eV/Å$^2$) | $1.50$ |
| $\kappa_\perp$ (eV/Å$^2$) | $9.14$ |
| $\psi_r$ (eV/Å$^2$) | $0.0$ |
| $\psi_{||}$ (eV/Å$^2$) | $9.34$ |
| $\psi_\perp$ (eV/Å$^2$) | $0.42$ |

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 $\sigma^2(B_{xy})$ are smaller than the size of the used symbols (open circles). The dashed line shows the in-plane boron lattice displacements in the CF model in the absence of the electron-phonon interaction.
eV/Å and $k_F \simeq \pi/12d_{B-B}$, where $d_{B-B}$ is the boron-boron distance.

The phonon dispersion and phonon density of states (PDOS) of our constant force model are shown in Fig. 4 in good agreement with the LDA calculations of Ref. 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 of the boron in-plane lattice displacements, with a better agreement with the experimental data. The increase of $\sigma^2_B(B_{xy})$ 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 $\sigma^2_B(B_{xy})$ is relatively weak. As we are going to see, the effects of the electron-phonon interaction are more apparent in the correlated pair motion.

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

Above we showed that the average uncorrelated thermal motions (equivalent to the Debye-Waller factor in crystallography) measured from MgB$_2$ are well explained by harmonic models with independent boron and magnesium motions. A strength of the PDF technique is that it is sensitive to correlations in the atomic dynamics that contain some additional details about the underlying interatomic potentials. Here we explore the motional correlations in the MgB$_2$ PDF data.

The Gaussian width $\sigma_{ij}$ of the PDF peaks is directly related to the mean-square relative displacement of atomic pairs projected onto the vector joining the atom pairs. Explicitly,

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

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

In our analysis, we focus on the width of the nearest neighbor boron-boron PDF peak, $(\sigma^2_{B-B})$, and on the nearest neighbor magnesium-boron peak, $(\sigma^2_{B-Mg})$. These are well resolved single-component peaks in the PDF whose width directly yields correlated dynamical information. The Gaussian widths $\sigma^2_{B-B}$, $\sigma^2_{B-Mg}$, as measured by the PDF data are shown in the upper panels of Fig. 4 (open circles) along with the same quantity evaluated within the CF model (solid line) according to the relation:

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

In this latter case in the right panel for $\sigma^2_{B-Mg}$ we have also added a small contribution of the local lattice displacements due to the disorder (see below for more details). Here we first note that, while the zero temperature values of $\sigma^2_{B-B}$, $\sigma^2_{B-Mg}$ are well reproduced by the CF model, this model is less good than was the case for the uncorrelated motions, especially at high temperatures.
The temperature dependence of the single-atom motions was well explained by the model, but not those of the correlated $\sigma^2_{ij}$, which suggests that the model is not capturing some aspect of the motional correlations. Introducing the electron-phonon coupling into the model improves the agreement slightly, with a larger effect observed on $\sigma^2_{\text{B-B}}$, 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. We note that the models are harmonic. Even in the case where we have introduced electron-phonon coupling, harmonic spring constants have been obtained from a fit to the LDA bands and we speculate that the discrepancy at high temperature is a result of anharmonicity in the boron motion.

As a general consideration, we would like to stress once more that while $\sigma^2(i_o)$ probes the absolute magnitude of the single atom mean-square displacement, $\sigma^2_{ij}$ provides information about the correlation between the lattice displacements of atom pairs. Let us consider for instance the case of $\sigma^2_{\text{B-B}}$ 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 $\sigma^2_{\text{B-B}} = 0$, while $\sigma^2_{\text{B-B}} = 2\sigma^2(\text{B}_{xy})$ when the nearest neighbor boron lattice displacements are uncorrelated, and $\sigma^2_{\text{B-B}} = 4\sigma^2(\text{B}_{xy})$ when they have opposite phase.

To formalize this we rearrange Eq. 10 as

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

Here the first two terms are related to mean-square thermal displacement of atoms $i$ and $j$ projected along $\mathbf{r}_{ij}$, 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:

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

where $\sigma^2_{ph}(i_j) = \langle \langle (\mathbf{u}_i \cdot \mathbf{r}_{ij})^2 \rangle \rangle$. Positive values of $\rho > 0$ describe a situation where the atoms move in phase, so that the resulting value of $\sigma^2_{ij}$ 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 $\sigma^2_{ij}$ larger than the uncorrelated case. It is important to note that the correlation function $\rho_{ij}$ in Eq. 10 expresses the degree of correlation between the total atomic displacements. In the presence of two different sources of lattice displacements (phonons and disorder), it is more convenient to split $\sigma^2_{ij}$ into a phonon and a disorder contribution. Assuming the local lattice displacements due to the disorder to be uncorrelated, we can write thus:

$$\sigma^2_{ij} = \sigma^2_{\text{ph}}(i_j) + \sigma^2_{\text{ph}}(j_i) - 2\sigma_{\text{ph}}(i_j)\sigma_{\text{ph}}(j_i)\rho_{ij} + \sigma^2_{\text{dis}}(i_j) + \sigma^2_{\text{dis}}(j_i), \quad (10)$$

where $\rho_{ij}$ represents now only the correlation between phononic lattice displacements.

Using Eq. 10, the correlation parameter can be calculated from the total width of the PDF peak as

$$\rho_{ij} = \frac{\sigma^2_{\text{ph}}(i_j) + \sigma^2_{\text{ph}}(j_i) + \sigma^2_{\text{dis}}(i_j) + \sigma^2_{\text{dis}}(j_i) - \sigma^2_{ij}}{2\sigma_{\text{ph}}(i_j)\sigma_{\text{ph}}(j_i)}. \quad (11)$$

Finally, the projected atomic mean-square displacements $\sigma^2_{ij}$ (lattice vibrations along the pair $\mathbf{r}_{ij}$ direction) can be related to $\sigma^2_{\alpha\alpha}$ (lattice vibrations along the Cartesian axes) by simple geometrical considerations. We have thus $\sigma^2_{\text{ph}}(\text{B}_{xy}) = \sigma^2_{\text{ph}}(\text{B}_{xz})$, $\sigma^2_{\text{ph}}(\text{B}_{yz}) = [4R^2\sigma^2_{\text{ph}}(\text{B}_{xy}) + 3\sigma^2_{\text{ph}}(\text{B}_{z})]/(4R^2 + 3)$, $\sigma^2_{\text{ph}}(\text{Mg}_{z}) = [4R^2\sigma^2_{\text{ph}}(\text{Mg}_{xy}) + 3\sigma^2_{\text{ph}}(\text{Mg}_{z})]/(4R^2 + 3)$, where $R = a/c = 0.88$ and where $a$ and $c$ are the in-plane and out-of-plane lattice constants. Similar relations hold true for the disorder contributions.

The phonon correlation factor $\rho_{ij}$ as extracted from the PDF data $\sigma^2_{\text{B-B}}$, $\sigma^2_{\text{B-Mg}}$, and from the single atom mean-square lattice displacements $\sigma^2(i_o)$ is shown in the lower panels of Fig. 6 (open circles), together with the corresponding correlation factor predicted by the CF model (solid lines). In order to extract the experimental value of $\rho_{\text{B-Mg}}$ we have taken into account a slight magnesium disorder along the $c$ axis, $\sigma^2_{\text{dis}}(\text{Mg}_{z}) = 0.0013 \AA^2$, in agreement with the previous analysis of the mean square absolute displacements $\sigma^2(i_o)$. We find a positive correlation factor for both $\rho_{\text{B-B}} \sim 0.1$ and $\rho_{\text{B-Mg}} \sim 0.1$, 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 (acoustic, low optical branch modes) are generally less intuitive explanation is that the in-phase phonon modes of displacements in this experimental probe. Positive values points out once more that all the motions are decoupled and the atoms are behaving largely like independent oscillators.

Another anomalous feature of MgB\(_2\) pointed out by this analysis is the lack of a temperature dependence for the correlation factors \( \rho_{ij} \) as compared with the CF model and with the standard behavior of other common materials. An increase of \( \rho_{ij} \) as function of temperature is indeed observed in many covalently bonded systems and it is essentially due to the fact that the thermal population of the low frequency in-phase phonon modes is larger than the high frequency out-of-phase phonon modes. The lack of this temperature dependence in our measurements can maybe be attributed to the anharmonic character of the high frequency (E\(_{2g}\)) B-B modes and it represents an interesting anomaly in this material whose physical interpretation can shed interesting light on the lattice dynamics in MgB\(_2\). Further work on this subject is required. As a final point, we can quantify in our model the role of the electron-phonon coupling on the correlation factors. As shown in Fig. 5 the inclusion of the electron-phonon interaction, which leads to a partial softening of the out-of-phase E\(_{2g}\) in-plane boron displacements, is reflected in a significant reduction \( \Delta \rho_{B-B} \sim -0.03 \) of the correlation factor \( \rho_{B-B} \) while a negligible effect is found on \( \rho_{B-Mg} \).

4 Conclusions

In this work we have investigated the local lattice properties of MgB\(_2\) 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 constant force model and a simple Einstein model. We have found that the constant force model as well as the Einstein one reproduce the average features of the lattice vibrations. This agreement suggests that boron and magnesium displacements, both in-plane and out-of-plane, are mostly independent of each other. 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. These results are in contrast with CF model which predicts correlation factors increasing with the temperature. This discrepancy supports the idea that anharmonic effects and strong decay processes for the E\(_{2g}\) B bond stretching modes are present, presumably due to the strong electron-phonon coupling.

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