Bonding Nature in a Novel Superconductor, MgB_2

In the beginning of the 21st century, a novel superconductor, MgB_2, was discovered by Akimitsu [1]. Because of its comparatively high Tc, 39 K, an anomalous number of experimental and theoretical studies were performed in order to gain an understanding of the mechanism of superconductivity. Since 1954 [2], it has been known that the crystal structure of this material is hexagonal (AlB_2 type, space group *P6/mmm*). The characteristic boron honeycomb sheets are sandwiched between the Mg triangular sheets like an intercalated graphite as shown in Fig. 1. The band structure calculations [3] predict the existence of a charge donation of two electrons from the ionized Mg to the boron conduction band while a strong B-B covalent bonding is retained. The superconductivity in MgB_2, which appears essentially to come about due to the metallic nature of the Boron 2-D sheets, has been interpreted as a phonon-mediated BCS-type mechanism. Such a two dimensional structure is a common feature in oxide superconductors as well as in intercalated graphite. The doping on the Mg site or Boron 2-D sheets was carried out to reveal the effect of the electron concentration on the superconducting temperature. Several reports of the loss of superconductivity have been presented for $Mg_{1-x}Al_xB_2$, $MgB_{1-x}C_x$, $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}Mn_xB_2$.

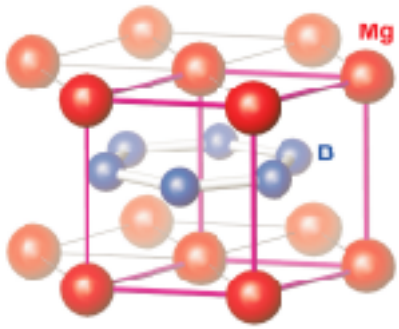

Fig. 1. Crystal structure of MgB_2.

The pressure evolution of the superconducting transition temperature was also reported and discussed for its relationship with the B-B and Mg-B bonding distances. However, the structural information used in the discussions was limited to the atomic level, *i.e.* lattice constants, bonding distance, etc. An experimental charge density would give a better understanding of how superconductivity links to the electronic and crystal structure of MgB_2.

In 2001, we reported on the precise charge densities of MgB_2 at R.T. and 15 K using synchrotron radiation powder data and presented experimental evidence for strong B-B covalent bonding, full ionization of Mg atoms at both temperatures as well as charge concentration on boron 2-D sheet at 15 K, which most probably relates to the superconducting mechanism [4].

The MgB_2 sample used in this work was prepared by Prof. J. Akimitsu. A pressed pellet of stoichiometric amounts of Mg and amorphous B was heated for 10 hours at 700 ℃ under an argon pressure of 196 MPa. The sample was found to be superconducting with T_c = 39 K. The granularity of the powder was reduced to a diameter even less than 3 microns by the precipitation method in order to obtain homogeneous intensity distribution in the Debye-Scherrer powder ring. The obtained powder sample was sealed in a silica glass capillary (0.3 mm int. diam.). The synchrotron radiation X-ray powder experiment with imaging plates (IP) as detectors was carried out by the Large Debye-Scherrer Camera at beamline **BL02B2** [5]. The He gas circulation type cryostat was used for the measurement at low temperature (Fig. 2). The X-ray powder patterns were measured at room temperature (R.T.) and 15 K(<<Tc). Both data were obtained under the same experimental conditions except for the temperature. The exposure time was 1 hour. The wavelength of incident X-rays was 0.6 Å. The X-ray powder pattern of MgB_2 was obtained with a 0.02° step from 9.0° to 65.0° in 2θ, which corresponds to 0.57 Å resolution in *d*-spacing.

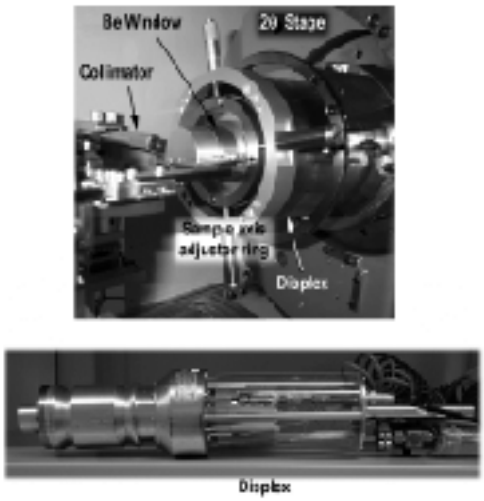

Fig. 2. The photograph of the displex installed in the Large Debye-Scherrer Camera.

The charge density distributions at both temperatures were visualized by the MEM/Rietveld method, which is a combination of the MEM and the Rietveld refinement [6]. This method has been successfully applied to the charge density studies of fullerene compounds, intermetallic compounds, α-boron, manganite, etc. For instance, the MEM/Rietveld method using synchrotron radiation powder data has revealed Mn $3d_{x^2-y^2}$ orbital order as a Mn-O bonding electron distribution associated with Mn(3*d*)-O(2*pσ*) hybridization at antiferromagnetic state in manganite, $NdSr_2Mn_2O_7$ [7]. In the present powder data, several weak impurity peaks were found and identified as MgO. The impurity MgO phase was also taken into account in the Rietveld pre-analysis. The space group was assigned to *P6/mmm* for both data at R.T. and 15 K. This implies that there is no structural phase transition from R.T. to 15 K. The results of the Rietveld refinement are shown for R.T. and 15 K in Fig. 3(a) and 3(b), respectively. The refined lattice parameters are listed in Table I. The weighted profile reliability factors of the Rietveld refinement as a pre-analysis for the MEM, R_{WP}, were 4.7% and 2.6% for R.T. and 15 K, respectively. And the reliability factors based on the integrated intensities, R_I, were 3.1% and 3.4% for R.T. and 15 K, respectively. In the analysis, the structure factors of the 55 reflections were derived from the observed integrated intensities. They were then used for further MEM analysis. Following the Rietveld pre-analysis, the MEM analysis was carried out by the computer program, ENIGMA [8], using 64×64×72 pixels. The reliable factors of the final MEM charge density were 1.7% and 1.5% for R.T. and 15 K, respectively.

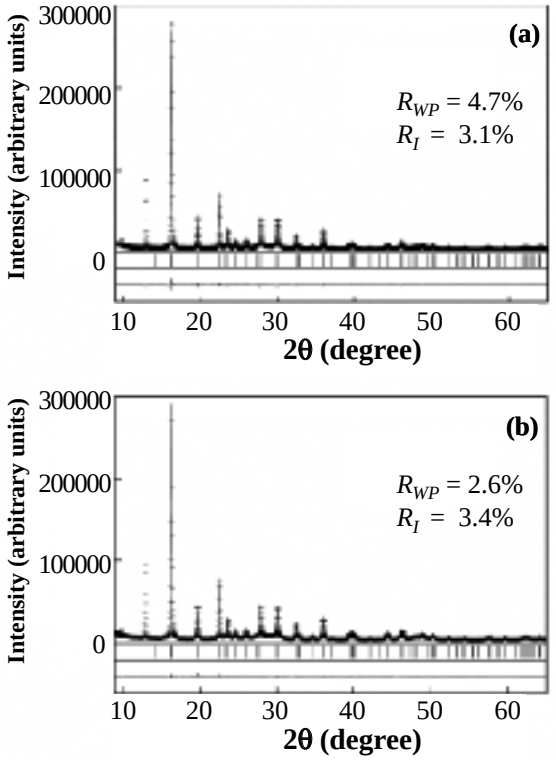

*Fig. 3. Fitting results of Rietveld analysis of MgB_2 at **(a)** R.T. and **(b)** 15 K.*

Table I. The lattice parameters and B-B, Mg-B atomic distances determined by the Rietveld analysis for MgB_2 at R.T. and 15 K.

	R.T.	15 K
Latice Parameter (Å)	a = 3.08831(3) c = 3.52415(8)	a = 3.08365(2) c = 3.51504(4)
B-B distance (Å)	1.78304(8)	1.78035(1)
Mg-B distance (Å)	2.50682(1)	2.50170(1)

A three-dimensional representation of the final MEM charge density at R.T. is shown in Fig. 4 as an equi-charge density surface. The equi-density level is 0.75 e/Å^3. The obtained MEM charge density clearly exhibits a strong covalent bonding network of boron 2-D sheet forming the six-membered rings, which are colored in blue. On the other hand, there is no localized electron density between Mg and boron atoms. In the interatomic region, electrons are distributed rather evenly similar to metal bonding. These characteristic density features are preserved in the charge density obtained at R.T. and consistent with the calculated band structures indicating the two band model [3]. Based on this model, several theoretical mechanisms of superconductivity have been proposed [9].

In Fig. 5, the MEM charge densities of the (110) sections containing Mg and boron atoms are shown for R.T. and 15 K with a structure model. The contour lines are drawn only for the lower density region. It is confirmed that there is no significant overlapping of the charge density around the Mg atomic sites. This is a high contrast to that of the boron-boron network. The MEM charge densities clearly reveal the boron-boron covalent bonding features. Although the change in the boron-boron interatomic distance is extremely small between R.T. and 15K as shown in Table I, the charge density values at the bond midpoints show the distinct different values, which are 0.9 and 1.0 eÅ^{-3} at R.T. and 15 K, respectively.

These values are in the range between those of Si (0.7eÅ^{-3}) [6] and Diamond (1.4 eÅ^{-3}) [6] and very close to the value of hexagonal-BN (1.0 eÅ^{-3}) [10].

The valence of the atom was examined by accumulating the number of electrons around a certain atom in the MEM density. So far, the valence of metal atoms encapsulated in metallofullerene has been determined experimentally from the MEM charge densities [6]. The number of electrons around an Mg atom was estimated as about 10.0(1)e and 10.0(1)e, respectively. These values are very close to the number of electrons of Mg^{2+} ion. This means that the Mg atoms are fully ionized in MgB_2 crystal at both R.T. and 15 K. On the other hand, the number of electrons belonging to the boron 2-D sheets show significant difference, they are 9.9(1)e and 10.9(1)e at R.T. and 15 K, respectively. This can be interpreted as the valence of the whole boron 2-D sheet changing from neutral to monovalent,

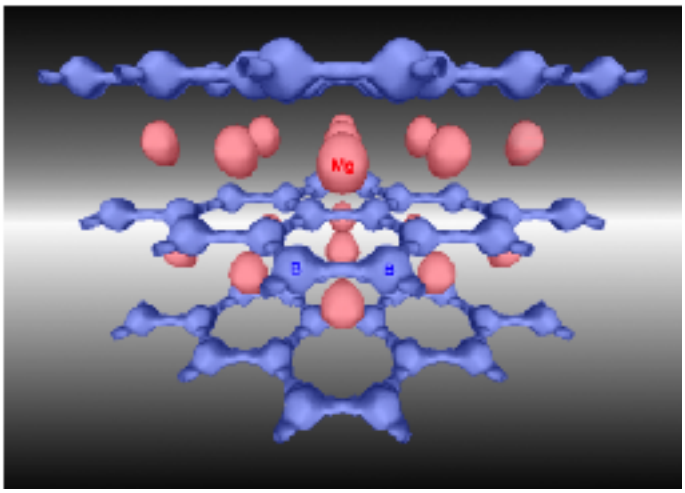

Fig. 4. The equi-contour (0.75 e/Å^3) surface of MEM charge density of MgB_2 at R.T.

i.e., $(B\text{-}B)^{-}$ at 15 K, which gives evidence of the increase of charge at the B-B bond midpoint at 15 K. Though the full charge transfer from Mg to boron 2-D sheets was expected to occur and form an isoelectronic sheet with graphite, no simple direct full charge transfer from Mg^{2+} to boron 2-D sheet was observed. The present results support the following scenario, that is, that the valence electrons are delocalized in the inter-atomic region at R.T., and half of them localized on the boron 2-D sheets at low temperature. This scenario implies the presence of electron transfer from the π bonds consisting of p_z orbitals to in-plain σ bonds consisting of p_{xy} orbitals in the two band model of MgB_2 at 15 K. Consequently, a subtle but important charge concentration on boron 2-D sheet at 15 K was found, which most probably relates to the superconductivity of this compound.

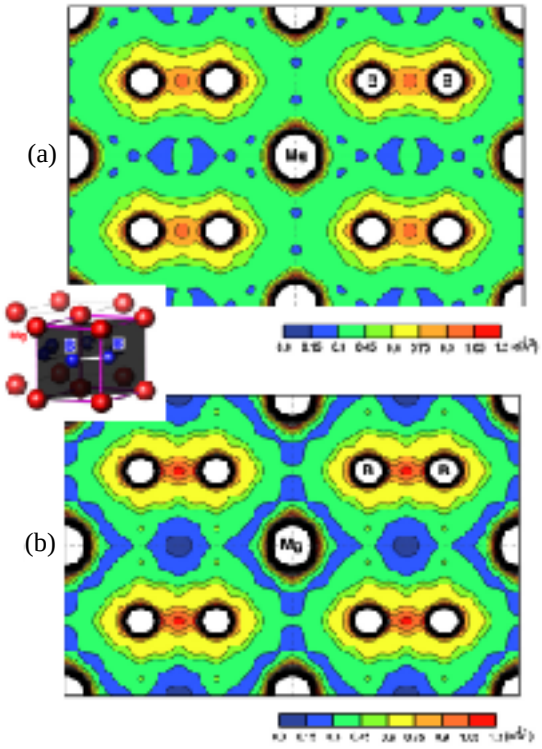

*Fig. 5. The (110) sections of the MEM Charge Density of MgB_2 at **(a)** R.T. and **(b)** 15 K with the schematic representation of the crystal structure. The contour lines are drawn from 0.0 to 3.9 at 0.15(e/Å^3) intervals for four unit cells.*

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