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Electron density distribution of α-gallium

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α-gallium is the most stable phase of gallium under the normal condition. The electron density distribution of α-gallium was obtained from X-ray diffraction data. Weak covalent bonds are observed in the (100) layer and interlayer bonds are weaker than intralayer bonds. Interlayer bonds are thought to be metallic bonds. This coexistence of two types of bonds is considered to cause the pseudogap structure of density of states.
Key words: electron density, gallium, X-ray diffraction, maximum entropy method, pseudogap

1. INTRODUCTION

Group III elements lay between the metal elements and non-metal elements in the periodic table. Hence, these elements are known for the peculiarity of chemical bonding. Especially, elemental gallium has some interesting properties. The elemental gallium at room temperature and atmospheric pressure is called α-gallium (α-Ga) This phase have very low melting point (300 K), though the boiling point of it is very high (2400~2600 K). This phase have peculiar crystalline structure as shown in Fig.1, distorted honeycomb structure. This structure can be thought as layer structure, and each gallium atom have only one nearest neighbour atom. Moreover, the electrical conductivity is anisotropic. *Ab initio* calculation attributed these strange properties to the covalent bonds between the two nearest gallium atoms. Calculated results showed the high electron density between the gallium atoms so that the nearest two gallium atoms make the covalent bonds to make dimmer like a "molecule" [1-3]. However, there are no experimental results to show any evidence of the existence of this covalent bond between the gallium atoms. We showed the electron density distribution (EDD) of the compounds based from group III element such as boron and aluminum [4, 5]. In this study, we obtained EDD of α-Ga experimentally using MEM/Rietveld analysis on the X-ray diffraction (XRD) data. Then we compare the experimental EDD with calculated EDD by FLAPW method. The density of states (DOS) of α-Ga has pseudogap structure (Fig. 2) [2,

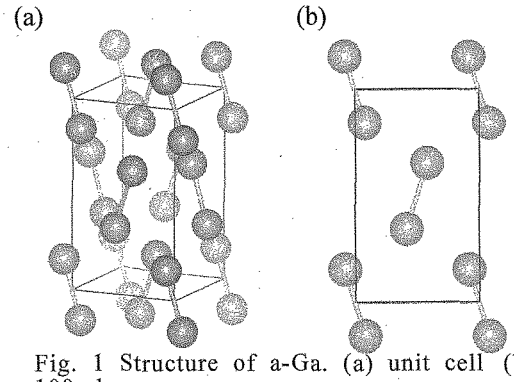

Fig. 1 Structure of a-Ga. (a) unit cell (b) 100 plane

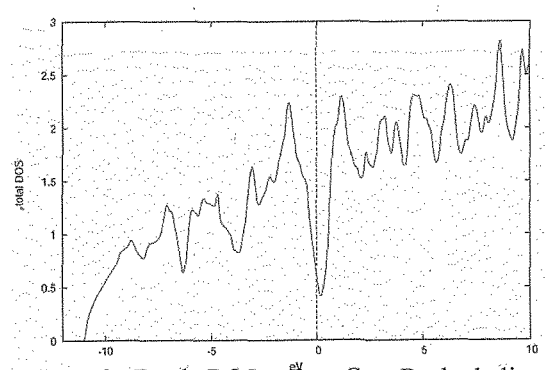

Fig. 2 Total DOS of α-Ga. Dashed line stands for the Fermi level. The pseudogap structure can be observed.

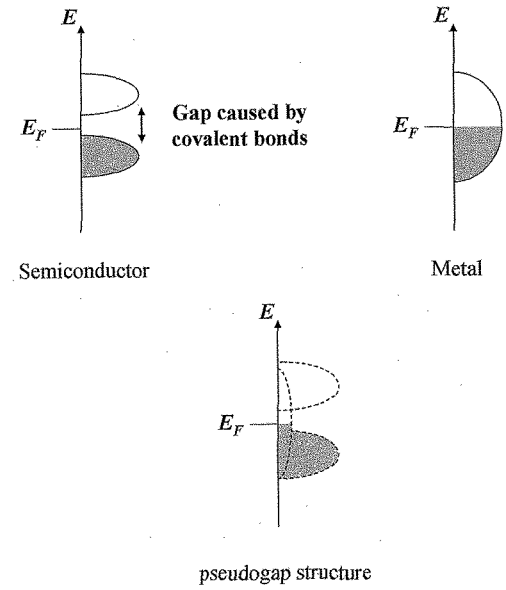

Fig. 3 Formation of the pseudogap explained by using the DOS. The coexistence of metallic and covalent bonds makes pseudogap structure.

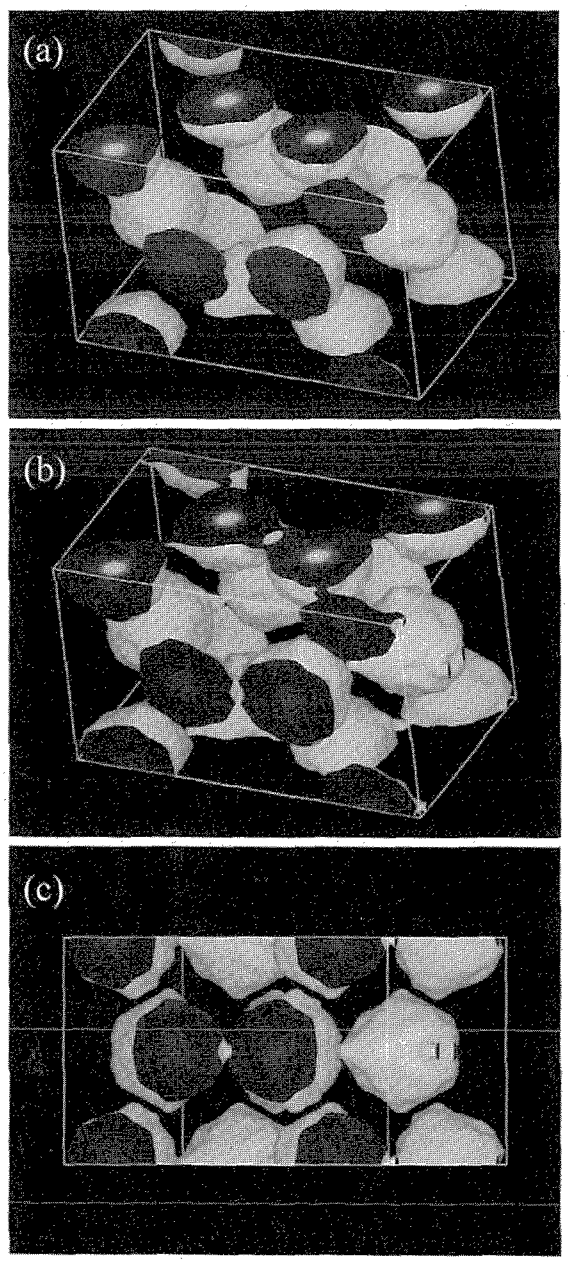

Fig. 4 EDD of α-Ga obtained experimental MEM analysis. (a) 0.40 e/Å^3 (b) 0.28 e/Å^3 (c) 0.28 e/Å^3 viewed fron 011 direction. Interlayer bonds cannot be observed.

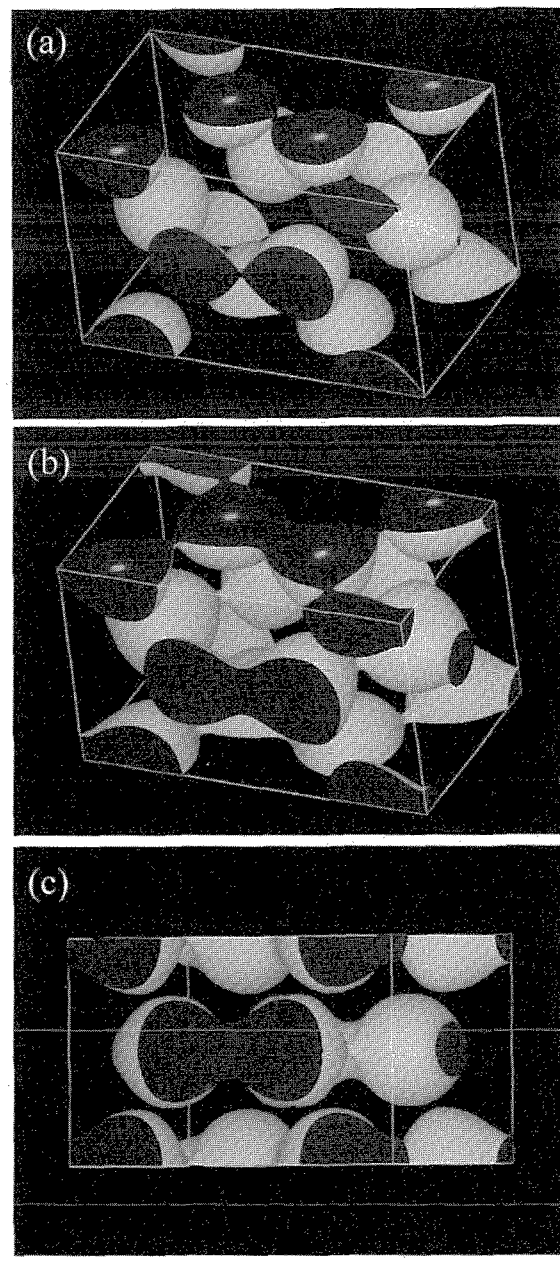

Fig. 5 EDD of α-Ga obtained ab initio calculation. (a) 0.40 e/Å^3 (b) 0.28 e/Å^3 (c) 0.28 e/Å^3 viewed fron 011 direction. The forms of EDD agree well with experimental result as shown in Fig. 4.

3]. We consider the coexistence of metallic and covalent bonds cause the pseudogap structure (Fig3). The aim of this study is confirmation of the coexistence of two types of bonds.

2. EXPERIMENTAL

α-Ga (Purity 4N) were cooled by liquid nitrogen because of low melting point and crushed and sifted to form powders with a grain size less than 20 μm. The samples were then ground with ice-cooled pestle and mortar. To collect the small grains and reduce the variation of the grain size, we floated the powder in a solvent and then dried the supernatant. By repeating this operation twice, we obtained samples with 1 μm grains. We confirmed that grains did not have anisotropy or size variation by ω-scanning. They were enclosed in a Lindemann glass capillary of 0.2 mm diameter. Then the powder XRD patterns were obtained in the 90 K nitrogen gas flow because of low melting point using a large Debye-Scherrer camera with an imaging plate (IP) at beamline BL02B2 at the SPring-8 synchrotron radiation facility. By setting the wavelength to 0.5 Å, XRD patterns were obtained from 0° to 75° in 2θ with a 0.01° step. This pattern was then analyzed by the MEM/Rietveld method.

First, the background corresponding to the halo from the glass capillary was subtracted from these patterns, and then each profile was fitted with a pseudo-Voigt

Table I Structure parameter of α-Ga obtained from Rietveld refinement.

α-Ga (Space group No.64) a=4.49067(2)Å b=7.64018(3)Å c=4.51854(2)Å				
site	x	y	z	B(Å^2)
Ga	0	0.1554(1)	0.0809(1)	0.365(5)

function to separate the overlapping structure factors.

The peaks of the unknown second phase were removed by fitting with a Pearson VII function. The number of crystalline structure factors used for MEM analysis as observed structure factors was 592.

After applying the Rietveld refinement, MEM analysis using the computer code ENIGMA [6] was carried out to obtain an EDD that was relatively unbiased by unobserved structure factors. MEM analysis was carried out using 48×76×48 pixels in an orthorhombic lattice. The resolution of the equidensity surface in the MEM analysis depends on the smallest d-spacing being used for analysis. In this research, it is 0.42 Å . The initial state used in the MEM analysis was a uniform distribution. To compare experimental and calculated results, then we calculated EDD and DOS using the ab initio calculation package Wien2k [7]. For the visualization of EDD equidensity surface, we used visualization program VESTA [8].

3. RESULTS AND DISCUSSION

The result of Rietveld refinement is shown in the Table I. The distance between the nearest neighbor atoms is 2.48 Å, second nearest atoms 2.68Å. Reliability factors of refinement R_{wp} and R_I are 1.65 % and 2.04 %, respectively. EDDs obtained from MEM analysis are shown in the Fig. 4. The electron density at the midpoint between the nearest neighbour atoms is 0.28 e/Å^3. However, the result of Bernasconi and coworkers insisted that the maximum charge density in gallium dimmer is 0.41 e/Å^3 [2]. To confirm the difference between experimental and calculated EDD, we calculated EDD by Wien2k code. The calculated EDD is shown in Fig. 5 the maximum density between nearest neighbour is 0.40 e/Å^3. It agrees with the previous calculational result well. However, the forms of coalent bonds agree with the experimental result, which have no maximum density between two gallium atoms. (Fig. 6) The covalent bond between gallium atoms is considered to be weaker than calculation. Weak covalent bonds also exist between second neighbour atoms on the same (100) plane. The density between interlayer atoms is 0.23 e/Å^3 for both experiment and the calculation, respectively. These bonds are weaker than intralayer bonds on (100) plane, and interlayer bonds have no directionality while intralayer bonds have strong directionality. Hence, interlayer bonds are metallic ones. The pseudogap of electronic structure shown in Fig. 2 is thought to be caused by this coexistence of metallic and covalent bonds.

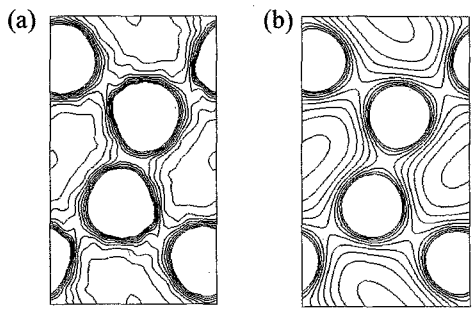

Fig. 6 Contour map of EDD on 100 plane obtained by (a) experiment (b) calculation. Minimum is 0.05 e/Å^3, maximum is 0.50 e/Å^3 and the step of contour is 0.05 e/Å^3.

The difference between experiment and calculation may be caused by temperature of the measurement. Because the melting point of α-Ga is very low, the 90 K is not low enough to ignore the thermal oscillation of each atom. Oscillation can average the EDD around the atom. If we analyze the data which is measured at lower temperature, the covalent bond between the nearest neighbour can be clarified more clearly.

4. CONCLUSION

We observed covalent bond on (100) plane in elemental gallium. However, that is observed weaker than calculation. Interlayer bonds are weaker than intralayer covalent bonds. These bonds are thought to be metallic bonds because of the absence of the directionality of the bonds. It is possible for coexistence of the two types of bonds to cause the pseudogap structure in the density of states.

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