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An Observation of Electron Density Distribution of Fe_3O_4

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Abstract. Magnetite, Fe_3O_4 , is a typical magnetic oxide with so called Verway transition at 124k. Its properties are very interesting in terms of magnetism, electric conduction, crystal phase transition, etc. While much thorough research has been done on Fe_3O_4 , a new experimental approach is needed. In order to obtain the electron density map with detail, a measurement of a lot of Bragg reflections is critical and hence the shortest wavelength is highly required.

We have developed an X-ray generator of $\text{W}\alpha$ ($\lambda=0.20889\text{\AA}$) radiation for this purpose and also, found the combination of the $\text{W}\alpha$ diffraction and Maximum Entropy Method (MEM) analysis produces a good result in obtaining not only the crystal structure but also the structure at the electron level. We have observed 615 reflections including one of index(hkl):(36 8 4) at the highest diffraction angle at room temperature. We observed the maps of the electron density distribution of the (100) and (110) planes of Fe_3O_4 in detail and also the 3d-localized electron density distribution corresponding to the d orbital..

I. Introduction

Fe_3O_4 is a typical magnetic oxide which has spinel type crystal structure. Its properties are very interesting in terms of magnetism, electric conduction and crystal phase transition. While much thorough research has been done on Fe_3O_4 , a new experimental approach is needed. A measurement of crystal structures on the electron level was carried out by the MEM software program analyzing the data of diffraction with short wavelength ($\text{W}\alpha$). This experimental approach seems to be novel and it was quite good to learn the electron structure. We have observed 615 Bragg reflections up to the index (hkl):(36 8 4) of Fe_3O_4 at room temperature and obtained the maps of the electron density distribution of the (100) and (110) planes in detail. And then, we further advanced the MEM analysis and found the sharp peaks corresponding to the localized electrons of the 3d orbital.

II Experimental Procedures

An already well known fact is the possibility of generating short wavelength characteristic X-ray from heavy elements such as W, Pt, Au, Th and U by using in-lab. X-rays. In practice, however, this has hitherto been virtually impractical because several improvements on the conventional techniques would be necessary. For instance, the excitation voltage for characteristic X-ray radiation is 69.3kV with W and 115kV with U. In order to obtain a more detailed electron density distribution, much shorter wavelength of X-ray radiation is highly required. We have newly developed a rotating-anode X-ray radiation of the $\text{W}\alpha$ ($\lambda=0.208892\text{\AA}$) on 200kV and max. 90mA which is the shortest wavelength for in-lab. X-ray diffractometer.

Recent works of the MEM were reviewed by M.Sakata et al. Here, we introduce information entropy, S. The unit cell is divided into $N_x N_y N_z$ pixels. ρ_i is the electron density at the pixel i, is deduced by maximizing the entropy which is as

$$S = - \sum_i \rho_i(x) \ln \rho_i(x) / m_i(x) \quad (1)$$

where $\rho_i(x)$ and $m_i(x)$ as $\rho_i(x) = \rho_i(x) / \sum_i \rho_i(x)$ and $m_i(x) = \tau_i(x) / \sum_i \tau_i(x)$, respectively. In the absence of any added information, the entropy, S is maximum when $\rho_i(x)$ is $m_i(x)$ for all i. Henceforward, the information entropy related to the electron densities by these equation. While $\rho_i(x)$ is a new electron density, $\tau_i(x)$ is a prior uniform electron density. In order to derive the MEM equation, the entropy term and the following equation (2) of the constraint term is combined by using Lagrange equation,

$$C = 1/N \sum_i \{ F_{\text{obs}}(h) F_{\text{cal}}(h) \}^2 / \sigma(h)^2 \quad (2)$$

here $\sigma(h)$ is the standard deviation of the observed $F_{obs}(h)$. This equation is expected to be 1 while we are taking the correct F_{obs} and F_{cal} of structure factors. When we are making of maximization of the entropy, it can be understood naturally that the electron distribution in the most ambiguous state are represented as a solution of the MEM within the error of measured data

The sample is a sphere of 0.86mm in diameter prepared from an Fe_3O_4 single crystal, which was grown in sealed air at 1640C by the Bridgeman method. The observed value(F_{obs}) obtained with 4-circle X-ray diffractometer compared with calculated value (F_{cal}). R-factor was below 1% and the agreement between the observed value and calculated value proved to be good. 615 Bragg reflections up to the index (hkl):(36 8 4) were observed.

III Results and Discussion

Fig. 1 shows the electron density distribution of the (110) plane of Fe_3O_4 . There is a bonding electron peak on the line connecting the oxygen and Fe^{3+} ion at the tetrahedral site(8a-site). This is corresponding to the covalent bond. The electron density distribution of Fe^{2+} , Fe^{3+} ions at the octahedral site(16d-site) and oxygen is linked by the outer electron cloud to be the ionic bond, appearing somewhat weaker than the covalent bond at 8a-site..

In Fig. 2 and Fig. 3 of the (110) plane and (100) plane, respectively, software program analysis of MEM can show the electron density distribution after the electron density of inner-shell electrons(core electrons) is subtracted. The contour line is drawn in a more minute way, at interval of $0.1e/A^3$. In Fig. 2, there is a electron density peak on the line connecting the oxygen and Fe^{3+} ions at the 8a-site which is corresponding to the covalent bond. And also, there are two sharp peaks on both proximate sides of the center of the Fe^{3+} ions at the 8a-site and Fe^{2+} , Fe^{3+} ions at the 16d-site. These peaks seem to be due to 3d localized electrons. It is considered to be the electron in d_y orbital of low energy state of 3d localized electrons, spreading in the direction of the space, not in the oxygen direction at the 8a-site. And also, at 16d-site, it is considered to be the electron in d_y orbital of high energy state of 3d localized electrons, spreading in the oxygen direction.

Fig1.;The electron density distribution of Fe_3O_4 (110) plane obtained by the MEM analyzing the data by Wka X-ray diffractometer. Contour lines are drawn at interval of $0.15e/A^3$.

Fig. 2; The electron density distribution of Fe_3O_4 .

(110) plane after the electron density of inner-shell electrons is subtracted. The contour lines are drawn at interval of $0.1e/A^3$.

Fig3.;The electron density distribution of Fe_3O_4 (100) plane after the electron density of inner-shell electrons is subtracted.

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References

- 1) K.Shiratori and Y.Kino; J.Mag. Mat. 20 (1980) 87
- 2) M.Sakata and N. Sato; Acta Cryst.A46 (1990)263
- 3) K.Yamamoto et al; Solid State Ionics 48 (1991) 241