EXAFS and XPS Study of Rutile-Type Difluorides of First-Row Transition Metals

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Abstract. Although most rutile-type difluorides (MnF₂, CoF₂ and NiF₂) have a positive thermal expansion coefficient, FeF₂ has a negative thermal expansion (NTE) along the c-axis in the high temperature region. In this study, we give an explanation of that behavior with Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Photoelectron Spectroscopy (XPS) techniques. From EXAFS results, it has become apparent that the length of the share-edge (Fe-Fe) of FeF₆ octahedra increased with the rise of temperature in the high temperature region. We have revealed that the force constant between nearest neighbor atoms (Fe-F) was much larger than that between second-nearest neighbor atoms (Fe-Fe) in FeF₂. In XPS measurements, it was discovered that the peak of F 1s of FeF₂ was located at the lowest binding energy position as compared to that of other difluorides. This means that the charge density around the F atom in FeF₂ was higher than that in other difluorides. It follows from this that the share-edge repulsive force in FeF₂ is larger than that in other difluorides. On account of the large repulsive force and the large force constant between nearest neighbor atoms, Fe atoms are attracted to share-edge with the rise of temperature.

Keywords: EXAFS, XPS, Rutile-type structure, First-row transition metal difluorides and NTE
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INTRODUCTION

The rutile-type structure has been studied for various materials repeatedly and with increasing accuracy over the years [1,2]. Many compounds which have the rutile-type structure are mostly dioxides or difluorides. First-row transition metal difluorides have been particularly studied from the standpoint of electronic and magnetic properties for a long time [1-10]. The rutile-type tetragonal unit cell (space group P4₂/mmm) contains two cations (A) at (0, 0, 0) and (1/2, 1/2, 1/2), and four anions (B) at (1 ± u, 1 ± u, 0) and (1/2 ± u, 1/2 ∓ u, 1/2). The rutile-type structure has edge-sharing octahedra (AB₆) which form chains along c-axis. The distance between second-nearest neighbor cations is equal to the length of the c-axis. Although most difluorides have a positive thermal expansion coefficient, iron difluorides (FeF₂) has a negative thermal expansion (NTE) coefficient along the c-axis in the high temperature region [11]. In our previous work [12], we could obtain detailed information about the interatomic distances and the thermal vibration of atoms in rutile-type difluorides by the analysis of EXAFS Debye-Waller factors. From the above results, we suggested that the second-nearest neighbor Fe-Fe atoms in FeF₂ vibrate with half phase shift to each other. As this vibrational mode increases among all thermal vibrational modes in the high temperature region, the second-nearest neighbor distance (the length of c-axis) decreases.

In this study, we have attempted to describe the reason for the NTE of FeF₂ by the combined use of refined EXAFS and XPS data from the standpoint of the crystal structure.

EXPERIMENTAL AND ANALYSIS

The EXAFS absorption spectra near the K-edge of the cations were measured in transmission mode in the temperature range from 20 K to 700 K at BL-7C of the Photon Factory in the High-Energy Accelerator Research Organization (KEK), Tsukuba. The positron storage ring current and energy were approximately 300 mA and 2.5 GeV, respectively. The synchrotron radiation was monochromatized with a Si (111) double crystal monochromator. The well-ground powder samples of MF₂ (M = Mn, Fe, Co and Ni) (Furuuchi Chemical Corporation; purity > 99.9%) had edge-jumps of 1 (Δμd), where μ and d are the linear absorption coefficient and the thickness of the
samples, respectively. The EXAFS interference function, \( \chi(k) \), was extracted from the measured absorption spectra using standard procedures [13], where \( k \) denotes the wave number of the photoelectron: 
\[
\chi(k) = \frac{2m(E - E_0)}{\hbar^2} \sqrt{2 E_E}.
\]
\( \chi(k) \) was normalized using MacMaster coefficients according to the EXAFS workshop report [14]. The programs XAFS93 and MBF93 [13] were employed for the data analysis to determine local structure parameters.

In the parameter fitting, the theoretical EXAFS function was filtered in the same way as the observed one in order to eliminate truncation effects through the Fourier transformation. The \( k \) range of the data used was 4-15 Å\(^{-1}\) and 4-12 Å\(^{-1}\) in the high and low temperature region, respectively. A double-shell fitting was carried out for the nearest neighbor distance in FeF\(_2\), because FeF\(_2\) is characterized by four coplanar Fe-F bonds more than 0.1 Å longer than two axial bonds in the Fe\(_6\) octahedron. The coordination number in FeF\(_2\) was fixed at the crystallographic value as \( N_1 = 2 \) and 4 corresponding to axial and coplanar bonds, respectively. A single-shell fitting was carried out for first-, second- and third-nearest neighbor distances in each material except for the first-nearest neighbor distance, Fe-F, in FeF\(_2\): the number of neighboring atoms was fixed at the crystallographic value as \( N_j = 6, 2 \) and 8 in the first-, second- and third-nearest neighbor atoms, respectively. The equal deformation of observed and calculated EXAFS functions improves the accuracy of the parameter fitting. The determined values of the distance and \( \sigma_j^{(2)} \) between the absorbing and backscattering atoms and more detailed analysis procedure were described in another paper [12].

Well-ground powder samples for X-ray Photoelectron Spectroscopy (XPS) were pressed into pellets 2-3 mm in thickness and about 5 mm in diameter. XPS analyses were carried out with an ESCA-1000AX spectrometer (Shimadzu Corporation) using monochromatized Mg-K\( \alpha \) radiation. The measurement range was from 680.0 eV to 700.0 eV for F 1s of all four samples. The binding energies of F 1s were corrected using 285 eV for C 1s as an internal standard.

**RESULTS AND DISCUSSION**

In the previous EXAFS measurement, we obtained the interatomic distances from metal ions (Mn, Fe, Co and Ni) to first-, second- and third-nearest neighbor atoms [12]. Figure 1 shows the temperature dependence of the interatomic distances of the second-nearest neighbor Fe-Fe in FeF\(_2\). From these data, we evaluated the deviation of the length of the share-edge F-F in FeF\(_2\) as shown in Figure 2.

In the derivation of the length of the share-edge, we used the following equation:
\[
R_{edge} = \sqrt{\frac{4(A - M_n)^2}{3} - (A - M_n)^2} - 2(A - F)
\]
(1)
where \( A \) is absorbing metal ion, \( M_n \) is \( n \)-th nearest neighbor ion and \( F \) is nearest neighbor fluorine ion. The length of the share-edge of MnF\(_2\), CoF\(_2\), NiF\(_2\) decreased monotonously with the rise of temperature. This is because that the increase rate in interatomic distances of the nearest neighbor ions is larger than that in the length of the \( a \)-axis. On the other hand, although the length of the share-edge of FeF\(_2\) decreased to 2.633(3) Å up to 200 K in the temperature range, it increased to 2.645(5) Å with the rise in temperature in the high temperature region (>200 K).
Figure 3 shows XPS spectra for F 1s of transition metal difluorides samples. Peaks in the XPS measurements on MnF$_2$, FeF$_2$, CoF$_2$ and NiF$_2$, attributed to F 1s as shown in Figure 3, were detected at approximately 685.0, 684.8, 685.2 and 685.3 eV, respectively. In the case of three samples of MnF$_2$, CoF$_2$ and NiF$_2$, it turns out that the values of binding energy of fluoride ions (F 1s) are almost increasing linearly with the increase in the atomic number of transition metal ions. This result means that the electron density around fluoride atoms decreases with the increase in the atomic number of transition metal ion, that is, the tendency of covalent bond is enhanced with the increase in the atomic number of transition metal. In other words, it can be said that electrons in the crystals of NiF$_2$ or CoF$_2$ tend to exist more locally than those of MnF$_2$.

On the other hand, FeF$_2$ is greatly shifted from the above tendency. That is, the fluoride atoms of FeF$_2$ have the tendency of ionic bond. The results, which were directly obtained from XPS measurement supports the force constants attracted from the EXAFS measurement results. It is reasonable to assume that as the charge density around F ions in FeF$_2$ is larger than that in other difluorides, the repulsion force between F-F of the share-edge in FeF$_2$ is larger than that in other fluorides. It is clear that this large repulsion force causes the increase of the length of the share-edge in FeF$_2$. It follows from this that the interatomic distance between the second-nearest neighbor ions (Fe-Fe), which has a relatively small force constant, decreases accompanying the lengthening of the share-edge (F-F) with increase in the high temperature region, despite the large force constant between the nearest neighbor ions (Fe-F) as shown in Table 1. It is concluded that this decrease of the second-nearest neighbor ions caused by the above reason corresponds to NTE in FeF$_2$.

**REFERENCES**