

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

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Abstract. Although most rutile-type difluorides (MnF_2 , CoF_2 and NiF_2) have a positive thermal expansion coefficient, FeF_2 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 FeF_6 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 FeF_2 . In XPS measurements, it was discovered that the peak of F 1s of FeF_2 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 FeF_2 was higher than that in other difluorides. It follows from this that the share-edge repulsive force in FeF_2 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 $P4_2/mnm$) contains two cations (A) at (0, 0, 0) and (1/2, 1/2, 1/2), and four anions (B) at $(1 \pm u, 1 \pm u, 0)$ and $(1/2 \pm u, 1/2 \mp u, 1/2)$. The rutile-type structure has edge-sharing octahedra (AB_6) 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 (FeF_2) 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 FeF_2 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 FeF_2 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 MF_2 ($M = \text{Mn, Fe, Co and Ni}$) (Furuuchi Chemical Corporation; purity > 99.9%) had edge-jumps of 1 ($\Delta\mu d$), 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: $k = [2m(E - E_0)/\hbar^2]^{1/2}$. $\chi(k)$ 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 $\text{\AA}^{-1}$ and 4-12 $\text{\AA}^{-1}$ 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 $\text{\AA}$ longer than two axial bonds in the FeF_6 octahedron. The coordination number in FeF_2 was fixed at the crystallographic value as $N_l = 2$ 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 α 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.

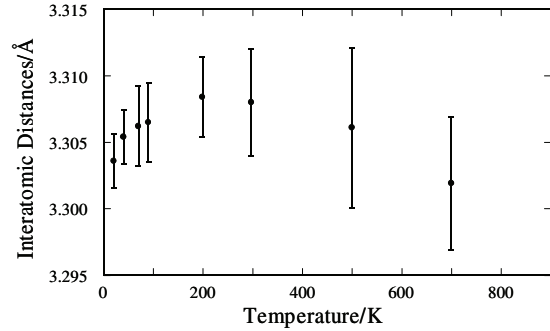


FIGURE 1. The temperature dependence of the interatomic distances of the second-nearest neighbor Fe-Fe in FeF_2 [12].

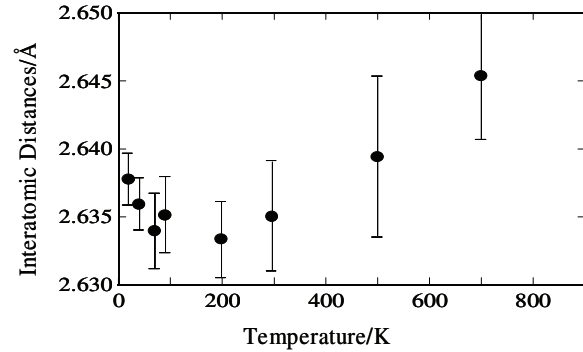


FIGURE 2. The temperature dependence of the length of the share-edge of F-F in FeF_2 .

In the derivation of the length of the share-edge, we used the following equation:

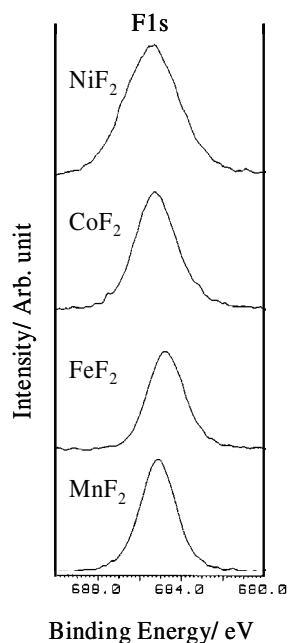
$$R_{edge} = \left\{ 4(A - M_3)^2 - (A - M_2)^2 \right\}^{1/2} - 2(A - F) \quad (1)$$

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) $\text{\AA}$ up to 200 K in the temperature range, it increased to 2.645(5) $\text{\AA}$ with the rise in temperature in the high temperature region (>200 K).

TABLE 1. Force Constants of MnF₂, FeF₂, CoF₂ and NiF₂ [12].

	Nearest Neighbor /eVÅ ⁻²	Second-Nearest Neighbor /eVÅ ⁻²	Third-Nearest Neighbor /eVÅ ⁻²
MnF ₂	5.55(13)	4.81(18)	3.29(14)
FeF ₂	8.09(40) (two-fold)	4.82(21)	3.33(10)
CoF ₂	7.46(25)	8.73(26)	5.56(27)
NiF ₂	7.83(83)	7.21(43)	4.15(20)

Figure 3 shows XPS spectra for F 1s of transition metal difluorides samples. Peaks in the XPS measurements on MnF₂, FeF₂, CoF₂ and NiF₂, 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 MnF₂, CoF₂ and NiF₂, it turns out that the values of binding energy of fluoride ions (F1s) 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 NiF₂ or CoF₂ tend to exist more locally than those of MnF₂.

**FIGURE 3.** XPS spectra for F 1s of MnF₂, FeF₂, CoF₂ and NiF₂.

On the other hand, FeF₂ is greatly shifted from the above tendency. That is, the fluoride atoms of FeF₂ 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 FeF₂ is larger than that in other difluorides, the repulsion force between F-F of the share-edge in FeF₂ 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 FeF₂. 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 FeF₂.

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