Po-031

Single-crystal structure analysis of spinel oxide FeV_2O_4 having orbital degree of freedom both in Fe and V ions

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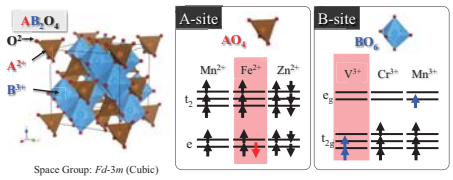
Introduction

◆ Crystal Structure of Spinel Oxide



Space Group: *Fd-3m* (Cubic)

◆ **Orbital** degree of freedom
◆ **Spin** degree of freedom
◆ Geometrical **Spin Frustration** in B-site (*pyrochlore lattice*)

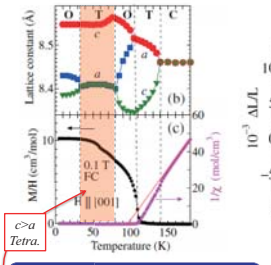
coupling → *Intriguing physical phenomena*

Various types of spinel oxides with orbital degree of freedom

AB_2O_4	JT-active ion	T_c (K)	Tetragonal distortion	AO_4 tetrahedron		BO_6 octahedron	
$FeCr_2O_4$	Fe^{2+} (d^6)	140	c<a $I4_1/amd$	compressed	$3z^2$-r^2 F-OO.	-	-
MnV_2O_4[1,2]	V^{3+} (d^2)	56	c<a $I4_1/a$	-	-	compressed	(xy,yz),(xy,zx) AF-OO.
ZnV_2O_4[3]	V^{3+} (d^2)	50	c<a $I4_1/amd$	-	-	compressed	(xy, yz+izx) F-OO.
Mn_3O_4 ($MnMn_2O_4$)	Mn^{3+}(d^4)	1443	c>a $I4_1/amd$	-	-	elongated	$3z^2$-r^2 F-OO.

◆ Characteristics of FeV_2O_4 spinel oxide [5]

1. Successive structural phase transition
(cubic-tetra–ortho-tetra-ortho)

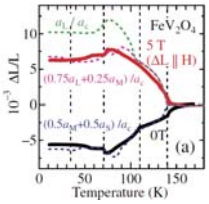


c>a Tetra.

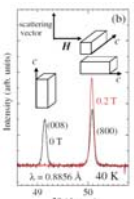
$FeCr_2O_4$, MnV_2O_4, ZnV_2O_4, MgV_2O_4 undergoes a structural transition with **c<a tetragonal structure**.
↓
c>a tetragonal structure is unique in FeV_2O_4

2. Magnetic-field-induced crystallographic domain switching

Temperature-dependence of strain

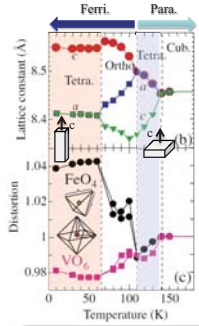


A synchrotron x-ray diffraction under *H*

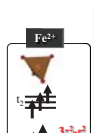


multidomain → *H* → LT tetra. (c > a) → c-axis of LT tetra. phase preferentially align along *H*

◆ Structure analysis (Polycrystal) [5]



Orbital state of Fe^{2+}



HT-tetra. (c<a)
Compressed FeO_4 $|3z^2\text{-}r^2\rangle$

LT-tetra. (c>a)
Elongated FeO_4 $|x^2\text{-}y^2\rangle$

What is the origin of the rich phase transition ???

Competition ? Cooperation

Fe^{2+} orbital ↕ spin — V^{3+} orbital ↕ spin

Purpose

Single-crystal structure analysis of FeV_2O_4

Determine the oxygen coordinates ↔ Strong electron-lattice coupling ↔ Orbital states of Fe, V ions

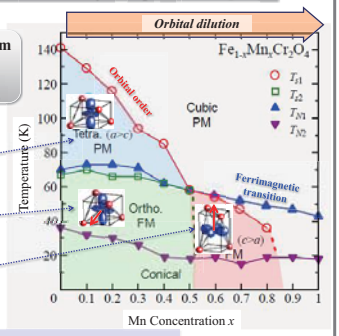
Experimental

◆ Crystal growth
- ✓ FeV_2O_4 and MnV_2O_4 (as a reference sample) single crystal : **Floating zone method in Ar atm.**
- ✓ Sample size: ~**20μm × 20μm × 20μm**

◆ Synchrotron x-ray diffraction
- ✓ Equipment: **Cylindrical IP camera in SPring-8 02B2**
- ✓ X-ray wave length: **λ= 0.3600Å**

◆ Appearance of *various orbital pattern* via a competition between *lattice anharmonicity* and *spin-orbit coupling* [4]

x-*T* phase diagram of A-site spinel $Fe_{1-x}Mn_xCr_2O_4$



$|3z^2\text{-}r^2\rangle$ type

$|3z^2\text{-}r^2\rangle + \delta|y^2\text{-}z^2\rangle$

$|x^2\text{-}y^2\rangle$ type

Lattice anharmonicity favors compressed FeO_4 $|3z^2\text{-}r^2\rangle$

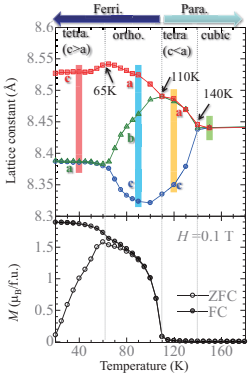
Competition

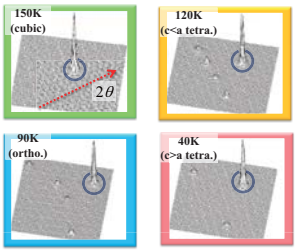
Orthorhombic distortion — orbital hybridazation $|3z^2\text{-}r^2\rangle + \delta|y^2\text{-}z^2\rangle$

$|x^2\text{-}y^2\rangle$ state is energetically favorable, considering *LS coupling*. $|x^2\text{-}y^2\rangle$

Results and Discussion

◆ Temperature dependence of lattice constants and three-dimensional plot of x-ray oscillation photographs at each phase in FeV_2O_4

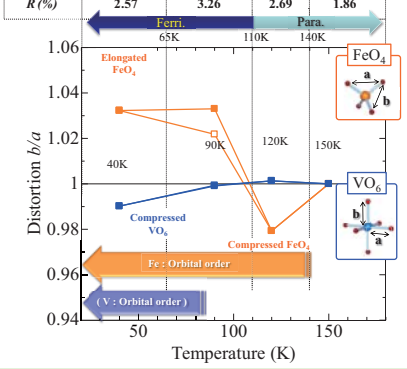




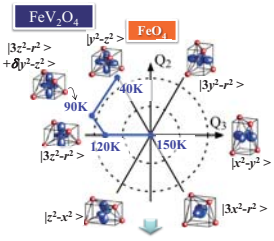
Almost single domain state was obtained in every phase, and we carried out single-crystal structure analysis using the most strong peak surrounded by a blue circle.

◆ Temperature dependence of distortion of FeO_4 and VO_6 in FeV_2O_4

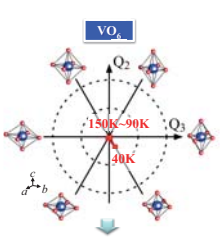
Crystal structure	c>a tetra.	ortho.	c<a tetra.	cubic
Space group	$I4_1/amd$	$Fddd$	$I4_1/amd$	$Fd\text{-}3m$
R (%)	2.57	3.26	2.69	1.86



◆ Q_2-Q_3 mode analysis of local distortion and the comparison between FeV_2O_4 and MnV_2O_4

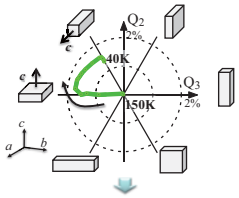


- 120K (tetra.) : $|3z^2\text{-}r^2\rangle$
- 90K (ortho.) : $|3z^2\text{-}r^2\rangle + \delta|y^2\text{-}z^2\rangle$
- 40K (tetra.) : $|y^2\text{-}z^2\rangle$



40K (c>a tetra.)
- Ferro orbital order ($|xy\rangle$, $|yz+izx\rangle$)[3] ?
- Orbital disorder?

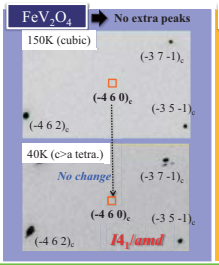
Q_2-Q_3 analysis of global distortion calculated using lattice parameter



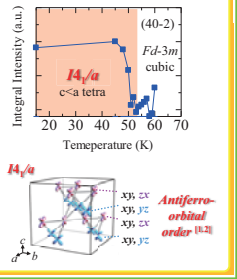
Global distortion almost corresponds to FeO_4 local distortion, suggesting FeO_4 distortion is more dominant than VO_6 one.

◆ Forbidden reflection by *d-glide symmetry operation*

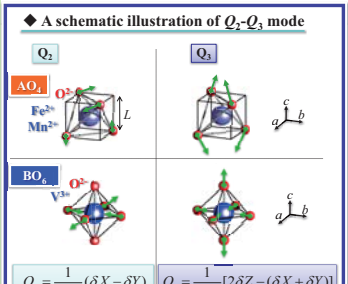
(*h*+*k*+*l* =4*n*+2 in cubic setting: **breaking of *d-glide symmetry***)

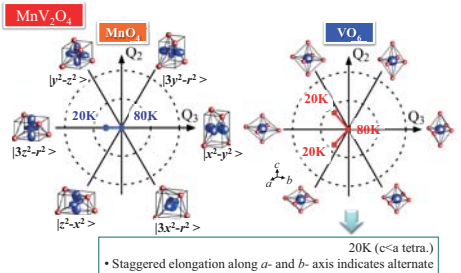


T-dependence of forbidden reflections



◆ A schematic illustration of Q_2-Q_3 mode

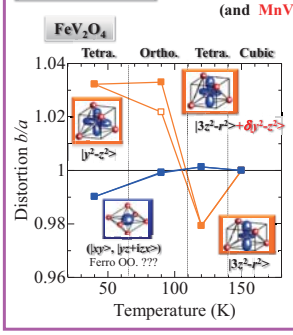




20K (c<a tetra.)
- Staggered elongation along *a*- and *b*- axis indicates alternate occupation of (*yz*, *xy*) and (*zx*, *xy*) orbitals along *c*-axis, and thus the formation of AF-orbital order.

Conclusion

We have carried out a single-crystal structure analysis of FeV_2O_4 (and MnV_2O_4) by means of synchrotron x-ray diffraction.



- **Orbital states of Fe^{2+} in FeV_2O_4 are determined, assuming strong electron-lattice coupling.**
- **Orbital order of Fe^{2+} occurs first and V^{3+} orbital order is considered to occur below 90K.**
- **Judging from the forbidden reflections, V^{3+} orbital state of FeV_2O_4 in 40K is considered to be ferroic one, whereas that of MnV_2O_4 is antiferroic one.**

References
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2. T. Suzuki *et al.*, Phys. Rev. Lett. **98**, 127203 (2007)
3. O. Tchernyshyov, Phys. Rev. Lett. **8** 157206 (2004)
4. S. Ohtani *et al.*, J. Phys.: Condens Matter **22**, 176003 (2010)
5. T. Katsufuji *et al.*, J. Phys. Soc. Jpn. **77**, 053708 (2008)