Studies of single-crystalline tetragonal tungsten bronze type $K_3Fe_5F_{15}$, a potential magnetoelectric material

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Abstract

Two phase transitions of $K_3Fe_5F_{15}$, at about 290 and 120 K, have been identified by polarized light microscopy and magnetic measurements on a single crystal grown from high temp. soln. with subsequent quenching from 973 K. The former one at about 290 K is a new second-order structural transition from the orthorhombic to a monoclinic phase, as shown by the appearance of new types of ferroelastic domain walls and a rotation of the optical indicatrix around the pseudo-tetragonal principal axis. The transition at about 120 K is second order and magnetic nature, accompanied by anomalies of spontaneous linear birefringence and antiferromagnetic type magnetic susceptibility. The temp. dependence of the magnetization suggests that a spontaneous ferromagnetic component appears in the magnetically ordered phase below 120 K.

Reference

STUDIES OF SINGLE CRYSTALLINE TETRAGONAL TUNGSTEN BRONZE TYPE $K_3Fe_5F_{15}$, A POTENTIAL MAGNETOELECTRIC MATERIAL

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Two phase transitions of $K_3Fe_5F_{15}$, at about 290 and 120 K, have been identified by polarized light microscopy and magnetic measurements on single crystals grown from high temperature solution with subsequent quenching from 973 K. The former one at about 290 K is a new second order structural transition from the orthorhombic to a monoclinic phase, as shown by the appearance of new types of ferroelastic domain walls and a rotation of the optical indicatrix around the pseudo-tetragonal principal axis. The transition at about 120 K is of second order and magnetic nature, accompanied by anomalies of spontaneous linear birefringence and antiferromagnetic type magnetic susceptibility. The temperature dependence of the magnetization suggests that a spontaneous ferromagnetic component appears in the magnetically ordered phase below 120 K.

Keywords: Tetragonal tungsten bronze type fluoride, $K_3Fe_5F_{15}$, mixed valency, phase transitions, polarized light microscopy, magnetization measurements.

INTRODUCTION

$K_3Fe_5F_{15}$ (KFEF), formerly formulated as $K_{0.6}FeF_3$, is one of the tetragonal tungsten bronze (TTB) type mixed valency fluorides, $K_xFe^{3+}_{2.5}Fe^{3+}_{1-x}F_3$ for $0.4 \leq x \leq 0.6$, which were synthesized in that structure for the first time by solid state reaction in 1965.¹ X-ray diffraction studies were performed on a KFEF single crystal and it was concluded that KFEF crystallizes in the orthorhombic space group Pba2 at room temperature.² Based on the atomic coordinates which were refined on a single crystal in the acentric space group Pba2, it was recently predicted that KFEF should be ferroelectric and ferroelastic at room temperature with a phase transition at about 535 K.³ Subsequently, it was reported that orthorhombic ferroelastic domains are present at room temperature and that there exists a phase transition to a prototype tetragonal symmetry at about 490 K, accompanied by a dielectric anomaly.⁴

We have synthesized stoichiometric single crystals of KFEF by high temperature solution growth with subsequent quenching from 973 K, according to the condition which was deduced from thermal analysis and X-ray diffraction measurements.⁵ After having established in a previous work the correlation between the refractive indices, extinction coefficients and the crystallographic axes at room temperature,⁶ we have undertaken in the present work optical and magnetic measurements on
single crystals of KFEF at low temperatures with a view to clarifying the phase sequence of KFEF and exploring potential magnetoelectric properties.

The appearance of new types of ferroelastic domain walls inside the orthorhombic ferroelastic domains has been observed. In addition to the phase transition at about 490 K, two other ones have been identified at about 290 and 120 K.

EXPERIMENTAL

Sample Preparation

Using a starting melt composition of KF = 38.71, FeF₂ = 38.71 and FeF₃ = 22.58 mole%, we have synthesized KFEF single crystals by high temperature solution growth, as described in References 5 and 6. By means of X-ray diffraction measurements on an orthorhombic single domain crystal the cell parameters were found to be \( a = 12.7451(7) \), \( b = 12.6466(6) \) and \( c = 3.9850(3) \text{Å} \) at 298 K. Using differential scanning calorimetry (D.S.C.), the transition temperature from tetragonal to orthorhombic symmetry was confirmed to be situated at about 490 K.

Single crystals were carefully selected under a microscope and separated from other phases by cleansing the surfaces. Making use of easy \{001\}_\text{orth} cleavage, a platelet of Type I, as illustrated in Figure 1, was prepared for the optical studies by carefully polishing to a thickness of 20 \( \mu \text{m} \), using alumina powder (\( \phi = 3 \mu \text{m} \)) and oil lubricant for avoiding any adsorption of water and herewith hydrolysis of the fluoride.

According to the optical studies of the orthorhombic ferroelastic domains at 298 K, summarized in Figure 1, the orthorhombic domain patterns of the platelet served for optical studies are shown in Figures 2 (a)-(c) and are schematically represented in Figure 2 (d).

Optical Studies

Polarized light studies were performed in transmitted light on a LEITZ Orthoplan Pol microscope in conjunction with a special He-flow cryostat (Oxford Instruments), adapted for optical measurements between about 7 and 300 K.

While the microscope was turned degree by degree around its axis from \(-10^°\) to \(+10^°\), the extinction directions of the new domains appearing below 290 K were analyzed by measuring the intensity of transmitted monochromatic light between crossed polars with a microphotometer installed on the microscope. The intensity measurements were performed on the measuring spots, A and B, corresponding to the two different orientations of the new domains originating from an orthorhombic single domain (Figure 3(c)). In the present studies, the crystal being fixed inside the cryostat, the polarization direction of the incident light was changed with respect to the crystal by turning the microscope around its optical axis by the angle \( \phi \). The polars were always kept mutually crossed and the starting position of \( \phi \) was set close to the extinction position of the orthorhombic ferroelastic domains at the beginning of the optical measurements.

High resolution spontaneous linear birefringence measurements by means of a
Principal Refractive Indices: \( n_\alpha (// b) < n_\beta (// a) < n_\gamma (// c) \)

FIGURE 1 Orthorhombic ferroelastic domain patterns of Type I, (a), (b) and (c), and Type II, (d), (e) and (f), and their schematic representations reproduced from Reference 6. The domain contrast exhibited in (a), (b) and (d) without analyzer is due to a remarkable anisotropic absorption (dichroism). The polarizer aligning with the common \( c \) axis, the domain contrast disappears in (f) without analyzer. See Color Plate IV.
FIGURE 2 The orthorhombic ferroelastic domain state of the Type I platelet (d = 20 μm): (a) between crossed polars, (b) without analyzer (dichroism), (c) between uncrossed polars at compensation with a tilting compensator (its γ-direction is indicated) and (d) schematic representation of the domain state. See Color Plate V.
FIGURE 3 New monoclinic ferroelastic domain patterns at 7.4 K appearing below 290 K inside an originally orthorhombic ferroelastic domain: (a) and (b) between crossed polars at extinction position of the domains corresponding to measuring spots A and B; \( \varphi \) stands for the angle of the rotation of the crossed polars with respect to the previous extinction position of the initial orthorhombic domains, while the crystal is fixed in the cryostat. (c) schematic representation of the monoclinic domains, indicating a rotation of the optical indicatrix around the orthorhombic \( c \) axis, the pseudo-tetragonal principal axis; the spots A and B shown in (c) indicate the areas on which the microphotometer measurements were performed. See Color Plate VI.

system combining a photoelastic modulator, a Babinet-Soleil compensator and a microphotometer\(^7\) were performed on the spot A (Figure 3 (c)) at different wavelengths (\( \lambda = 555, 589, 630 \) and 740 nm) upon heating from 10 to 300 K at a rate of +3 K/min. The exact order of compensation had been identified in advance by the analysis of the interference order established according to Beugnies\(^8\) and the spontaneous linear birefringence was determined by measuring the path difference at 7 K in the same configuration at each wavelength.

**Magnetic Measurements**

By means of a Vibrating Sample Magnetometer (EG&G PAR model 155), the field dependence of magnetization was measured between -17 and +17 kOe upon
heating at several temperatures and the temperature dependence of magnetization at $H = +17$ kOe was obtained. The measurements were performed on a powder sample of crushed single crystals of 93.7 mg both with ($H = 9$ kOe) and without a magnetic field cooling from 300 to 4.2 K.

In order to clarify the magnetic nature of KFEF at low temperatures, magnetic measurements by means of a SQUID magnetometer were carried out on a twinned single crystal of 1.2 mg along the pseudo-orthorhombic c axis which has a common orientation for the two orientation states of the orthorhombic ferroelastic domains, as well as for the four ferroelastic domain states of the monoclinic phase (see below). The temperature dependence of the magnetization was measured in detail at a constant field of $H = 10$ kOe, with a preceding magnetic field cooling from 300 to 5 K in a field of $H = 10$ kOe. With a view to identifying either ferromagnetic or ferrimagnetic type ordering below 120 K, the field dependence of magnetization was also measured up to 55 kOe below 150 K. In order to derive the spontaneous magnetization and the magnetic susceptibility, the calculus was carried out on the data measured at $H \geq 3$ kOe by a method of least squares, according to the equation:

$$M = M_0 + \chi \cdot H,$$

where $M$ and $M_0$ stand for the total and spontaneous magnetization and $\chi$ and $H$ for the magnetic susceptibility and magnetic field, respectively.

RESULTS AND DISCUSSION

As shown in Figures 3 (a) and (b), new types of ferroelastic domain walls were found to appear upon cooling with crossed polars close to the extinction positions

![Figure 4](attachment:image.png)

**FIGURE 4** Temperature dependence of the angular difference in extinction position between the spots A and B, $\varphi_{ext}(A) - \varphi_{ext}(B)$, measured at $\lambda = 670$ nm, indicating a rotation of the optical indicatrix due to the monoclinic inclination.
of the orthorhombic domains, exhibiting new domain patterns developed inside the initial orthorhombic ferroelastic domains. The contrast of the new domain patterns interchanged when the crossed polars were turned in the opposite senses with respect to the previous extinction direction of the orthorhombic domains. According to the orthorhombic domain orientations (Figure 2(d)), it was revealed that the new ferroelastic domain walls run along the orthorhombic a and b axes in the initially orthorhombic domains.

The extinction directions of the new domains were identified from the intensity minima by the intensity measurements, while rotating the microscope with fixed crossed polars around its axis. Figure 3(c) shows that the extinction directions of the two new domains rotate in opposite directions with respect to the initial extinction direction of the orthorhombic domains, forming an angle of $1.8^\circ$ ($\lambda = 670$ nm) with each other at 7.4 K.

As shown in Figure 4, the temperature dependence of the difference in the extinction position between the spots A and B, $\varphi_{\text{ext}}(B) - \varphi_{\text{ext}}(A)$, indicated that a second order structural phase transition occurs at about 290 K. Judging from that rotation of the optical indicatrix and from the strong dispersion of the extinction position below 290 K (Figure 5), it was concluded that the crystal symmetry changes from orthorhombic to monoclinic at about 290 K.

On the other hand, another phase transition was identified distinctly at about 120 K by means of high resolution spontaneous linear birefringence measurements. As shown in Figure 6(a), the spontaneous linear birefringence measured at different wavelengths showed an anomaly at $T_1 = 121 \pm 2$ K independently of wavelength and exhibited strong dispersion below and above $T_1$. The spontaneous linear birefringence measured at $\lambda = 740$ nm was less sensitive to the anomaly than at the other wavelengths. In order to clarify the nature of the observed anomalies in detail, an additional measurement at $\lambda = 630$ nm was performed with the same set-up between 80 and 150 K, upon heating and cooling at the same rate of $\pm 3$
K/min. Figure 6 (b) shows that the anomaly at $T_1$ is reproducible and reversible in the thermal cycle. This anomaly can be attributed to the onset of a magnetic ordering at $T_1$, as is discussed below.

Figures 7(a) and (b) show the temperature dependence of the total magnetization measured both on a powder and on a twinned single crystal and that of the inverse magnetic susceptibility derived from the total magnetization along the orthorhombic $c$ axis of a twinned single crystal, respectively. It was supposed that an antiferro-
FIGURE 7 Magnetic measurements upon heating: (a) Temperature dependence of the total magnetization measured on a powder sample and on a twinned single crystal along the orthorhombic c axis; the crosses and the triangles, × and Δ, represent the magnetization of the powder sample measured by a Vibrating Sample Magnetometer, with and without magnetic field cooling at $H = 9$ kOe from 300 to 4.2 K, respectively; the circles, O, represent the magnetization of the twinned single crystal measured by a SQUID magnetometer after magnetic field cooling from 300 to 5 K at $H = 10$ kOe along the c axis. (b) Temperature dependence of the inverse magnetic susceptibility measured on a twinned single crystal along the orthorhombic c axis by means of a SQUID magnetometer; the solid diamonds, *, were derived from the field dependence of the total magnetization measured at $H \approx 3$ kOe by a least squares method using the equation (1) (in the text); the diamonds, o, were calculated from the total magnetization, M (shown in (a)), measured at $H = 10$ kOe, according to the equation: $1/\chi = H/M$. 
magnetic type ordering would take place at about 120 K and that a weakly ferromagnetic phase would exist below 120 K. As shown in Figure 8, the temperature dependence of the spontaneous magnetization along the orthorhombic c axis, deduced from the field dependence of the total magnetization by extrapolation to zero field, corroborated the suggestion of a weakly ferromagnetic or ferrimagnetic phase and confirmed that there exists a magnetic phase transition at about 120 K. According to the correspondence between the anomalies of the spontaneous linear birefringence and the spontaneous magnetization, we concluded that the magnetic phase transition at about 120 K is of second order.

However, we could not observe any saturation of magnetization or any hysteresis loop below 120 K, as the magnetization measured in the present work was proportional to the magnetic field up to 55 kOe even at 5 K. As far as the magnetic properties of KFEF are concerned, we expect a more complicated spin ordered state in the low temperature phase rather than a simple collinear antiferromagnetic ordering. This point of view is suggested by a triangular arrangement of the iron ions, Fe$^{2+}$ and Fe$^{3+}$, in the TTB type crystal structure, giving probably rise to frustration phenomena in spin ordering.

CONCLUSIONS

In the present paper, besides the formerly reported phase transition at about 490 K from tetragonal to orthorhombic symmetry, the identification of two other phase transitions is described. One of them is a new second order structural transition at about 290 K from the orthorhombic to a monoclinic phase, as shown by the appearance of new types of ferroelastic domain walls and by the rotation of the optical indicatrix around the pseudo-tetragonal principal axis resulting from the monoclinic inclination. The second one is of magnetic nature and occurs at about 120 K,
accompanied by the anomalies of the spontaneous linear birefringence, the anti-
ferromagnetic type magnetic susceptibility and the onset of a weak spontaneous
magnetization.

In order to identify the magnetically ordered low temperature phases of KFEF
in more detail, further investigations are required. In particular nuclear and mag-
netic structure determinations, as well as magnetic and magnetoelastic measure-
ments on orthorhombic and monoclinic ferroelastic single domains are desirable.

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COLOR PLATE IV. See S. Ishihara. Figure 1.
FERROELECTRICS, Volume 162(1-4).
COLOR PLATE V. See S. Ishihara, Figure 2.
FERROELECTRICS, Volume 162(1-4).
COLOR PLATE VI. See S. Ishihara, Figure 3. 
FERROELECTRICS, Volume 162(1–4).