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STRUCTURAL PHASE TRANSITIONS IN $KTiF_4$

By

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Abstract: *Phase transitions in the $KTiF_4$ single crystals are observed by electron diffraction. These transitions are attributed to the rotation of TiF_6 octahedra about their principle axes. In this way changes of the unit cell can occur as well as diffuse scattering due to LRO and SRO of the oscillations.*

1. INTRODUCTION

The structure of KMF_4 (M = Ti, V, Fe) is based on two - dimensional layers of corner - linked MF_6 octahedra. The ideal structure of $KTiF_4$, which is similar to the structures of $KFeF_4$ and KVF_4, is shown in Fig. (1), where the TiF_6 octahedra are not tilted about any axis. The array of octaedra is successively translated by 1/2 b in the (001) planes. Structural phase transitions of these compounds have been studied by means of dielectric constant measurements and X-ray diffraction methods[1,2].

On cooling the compounds from the disordered phase a series of new phases results, attributed to the tilting of the MF_6 octahedra about their principle axes. Weak superlattice reflections are observed by X-rays indicating changes of the unit cell. In addition, the crystals are fragmented into domains. Different domains can contribute in the diffraction patterns simultaneously. At room temperature, the superlattice reflection indicating doubling of the unit cell of the ideal structure in the b direction are few and very weak compared to the superlattice reflections suggesting doubling of the unit cell in the a direction. If these very weak reflections are ignored the room temperature structure is based on the unit cell with lattice constants a = 7,596 Å, b = 3.884 Å, c = 12.27Å, z = 4 and space group A_{mma}[1]. If the very weak reflections are considered the structure is based on the unit cell with lattice constants a = 7.76 Å, b = 7.96 Å, c = 12.20 Å, z = 8 and space group P_{mmn}[2].

We report the results of structural transitions of $KTiF_4$ using the electron diffraction method which is more suitable for selecting a single domain diffraction pattern. This method will provide new interesting results about the superstructures and oscillation modes.

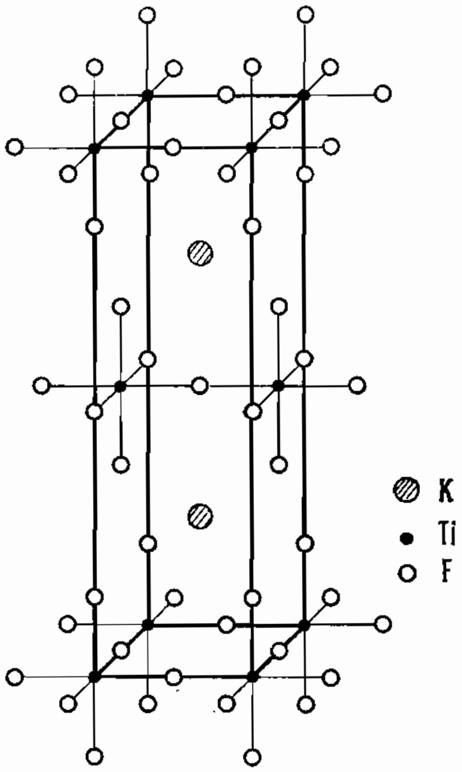


Fig. 1. Ideal structure of $KTiF_4$.

2. EXPERIMENTAL

2.1 CRYSTAL PREPARATION

Single crystals of $KTiF_4$ were grown from the melt. Compounds of commersial purity were used as starting materials (KF, TiF_4, Ti and NH_4HF_2). It was necessary to use reducing conditions in order to eliminate any oxygen and water impurities. This was achieved by the decomposition of NH_4HF_2 which produces HF. The starting materials were closed in a graphite crucible provided with a lid and then put inside a long inox tube closed at both its ends. Two tubes with smaller diameters were fitted at the top and the bottom faces of the former tube in order to permit the flow of dried, deoxygenated nitrogen. Finally the system was put in a vertical furnace open at both ends.

The materials were heated at 900 °C and then slowly cooled down to 500 °C with a cooling rate of 3 °C/h. During the cooling period a continuous flow of nitrogen was maintained.

2.2 ELECTRON DIFFRACTION

The layer structure of $KTiF_4$ is particular suitable for preparation of thin specimens for diffraction studies by means of transmition electron microscope. It is possible to cleave the crystals by repeated use of adhesive tape. The electron diffraction studies have special characteristics as following:

1) perfect monochromatized beam
2) ability to change the beam width ($<1\mu m$)
3) short exposure time for taking a photograph ($<$min).

It is possible, therefore, to study the short range correlation of the microstructure by observing the diffuse reflection in the critical region near the structural transition point.

A Jeol 100C electron microscope was used operated at an accelerating voltage of 100KV and provided with a heating holder.

Figure (2) shows the diffraction patterns taken at room temperature. Figure (2a) is taken with the electron beam along [001] direction while Fig. (2b) and Fig. (2c) are taken by tilting the crystals around [100] and [010] respectively. Indexed diffraction patterns, based on the superlattice unit cell, are also included in Fig. (2). Only superlattice reflections of the type $h + k = 2n$ are present in the basic section. The reflections of the type h00 and 0k0 ($h,k = 2n + 1$) are absent in the [001] section and can only appear in the tilted sections as a result of double diffraction.

Fig. (3) shows the basic section at 250 °C of the same crystal region as in Fig. (2). Now diffuse intensity lines also appear in directions parallel with [100] and [010]. The intensity of the lines is strong when they pass throug the h00 reflections ($h = 2n$) and very weak when they pass through the reflections h00 ($h = 2n + 1$) and 0k0 ($k = 2n$). There are no diffuse lines through the reflections 0k0 ($k = 2n + 1$). Fig. (3) now contains strong basic reflections of the type h00 ($h = 2n$) and 0k0 ($k = 2n$) in contrast to Fig. (2) where the 0k0 ($k = 2n$) re-

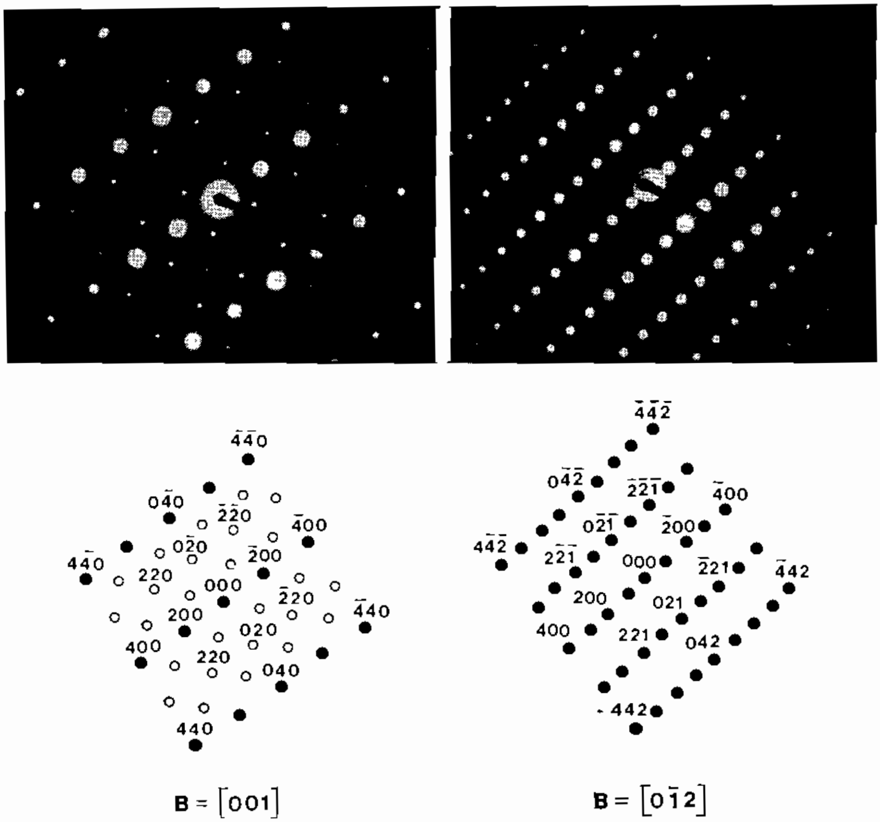


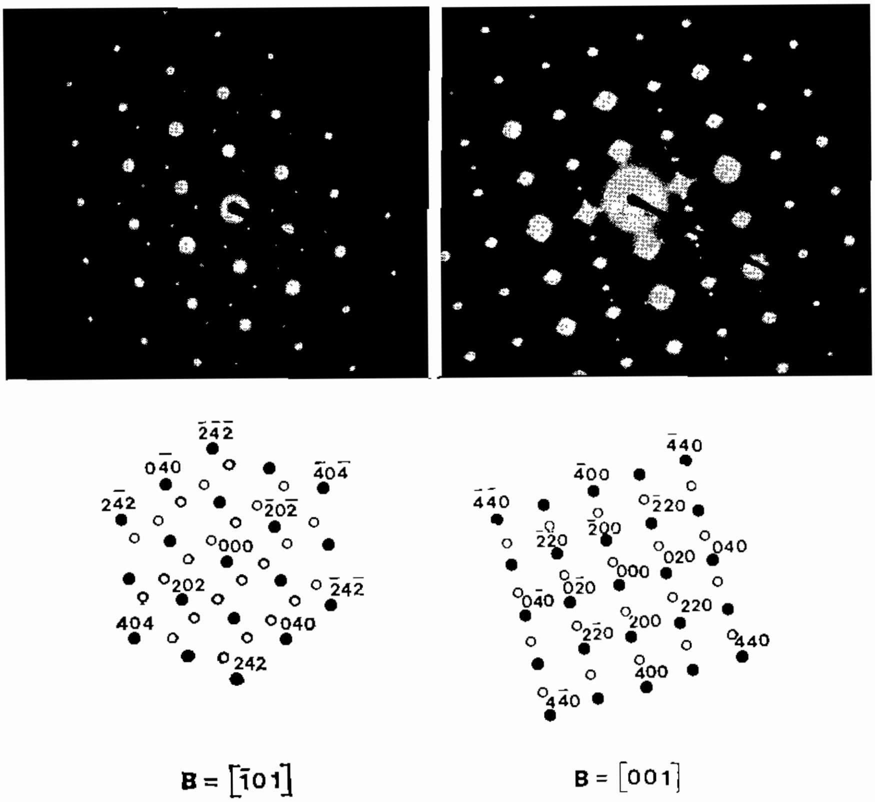
Fig. 2. Diffraction patterns of the room temperature phase; beam directions
a) B= [001]
b) B= [0$\bar{1}$2]
c) B= [$\bar{1}$01]

flection is very weak. The hk0 reflections with h + k = 2n are absent at 250 °C but the h00 reflections (h = 2n + 1) are present in the [001] section.

3. DISCUSSION

The electron diffraction studies provide the following results about the unit cell of $KTiF_4$ at different temperatures.

a) At room temperature, both the a and b axis of the disordered phase are doubled as is evident from Fig. (2). This is in agreement with the



Fif. 3. Diffraction pattern of thc high temperature phase; beam direction B=[001[.

face centred unit cell proposed by Hidaka et al[1] for the room temperature phase of $KTiF_4$.

b) Above 215°C the unit cell is changed. Now only the a axis of the ideal structure is doubled. This unit cell is also in agreement with the unit cell proposed by Hidaka et al.[1] for the phase observed above 215 °C. Also the systematic extinctions of reflections observed by electron diffraction are in agreement with the space groups proposed for the two phases[1].

The diffuse intensity lines, for first time observed by electron diffraction in $KTiF_4$, have some common characteristics with the diffuse lines observed in $CsVF_4$[3]. This compound has a similar layer structure with $KTiF_4$, i.e. layers of cornerlinked octahedra of VF_6. The octahedra of different layers, however, have common principle axis along the c - direction without any shift of the layers relative to each other. In $KTiF_4$ the successive layers are shifted by 1/2b and the c axis is doubled. Thus, it is expected a different behaviour of rotation of octahedra about their principle axes in the two compounds. In fact, the diffuse lines observed in $KTiF_4$ and $CsVF_4$ have some different characteristics, i.e. no diffuse lines or any satellite reflections along <110> directions are observed in $KTiF_4$, while they are observed in $CsVF_4$ below 250 °C.

However, the diffuse lines observed in $CsVF_4$ above 250 °C and in $KTiF_4$ also have some similar characteristics. The diffuse lines in both materials parallel with the [010] direction have alternately strong and weak intensity when they pass through the h00 reflections with $h = 2n$ and $h = 2n + 1$ respectively. The diffuse lines parallel with the [100] direction have strong (weak) intensity when they pass through the 0k0 reflections with $k = 2n$ in $CsVF_4$ ($KTiF_4$) and weak (zero) intensity when they pass through the 0k0 reflections with $k = 2n + 1$ in $CsVF_4$ ($KTiF_4$).

The diffuse scattering in $CsVF_4$ was explained on the basis of the short range ordering of the oscillations of the VF_6 octahedra about their principle axis[3]. An oscillation mode can be represented by ($n_i + \varepsilon_i$, $n_j + \varepsilon_j$, $n_k + \varepsilon_k$). Here n_i means a SRO of the phase being along [100] for an oscillation of octahedra around [100] and ε_i means an amplitude of the oscillation around [100]. For an example, the rotation of octahedra around [010] is represented by $(0, n_j + \varepsilon_j, 0)$. The value of $n = 0$ or 1/2 means that the phase of oscillation is in phase or in antiphase respectively.

The diffuse lines observed at the high temperature phase of $KTiF_4$ can be related to two kinds of modes with representations $(n_i + \varepsilon_i,0,0)$ an $(0,n_j + \varepsilon_j,0)$. If there is a coupling between them, the representation will be $(n_i + \varepsilon_i,n_j + \varepsilon_j,0)$. However, these modes are not coupled with each other in $KTiF_4$ as it can be deduced from Fig. (3) where only diffuse lines along [100] and [010] are present. There is no diffuse line along [110] or [$1\bar{1}0$].

In the high temperature phase of $KTiF_4$, the amplitude of rotation of octahedra around [100] is zero according to Hidaka et al.[1]. Fig. (3) suggests that this amplitude is not exactly zero but there is a SRO of rotation along [100]. In the [010] direction the amplitude of rotation is not zero, in agreement with Hidaka et al.[1]. The presence of the superlattice reflection 100 is due to the in phase coupling of the oscillation of octahedra around [010] resulting in a doubling of the [100] axis of the disordered phase. In addition, there is a SRO along [010] for the oscillation of octahedra around [010] resulting in diffuse lines along [010]. Thus, the rotation of octahedra around [100] and [010] shows different characteristics in agreement with the structure of $KTiF_4$.

On the other hand, the room temperature phase of $KTiF_4$ shows no diffuse lines. This means that the transition from the high temperature to the room temperature phase induced the coupling of oscillation of octahedra around and along [100] and [010]. Since the superlattice reflection 110 now appears, it is obvious that the LRO of rotation of octahedra along and around [100] and [010] prevails resulting in doubling of both a and b axes of the disordered tetragonal phase.

Our present work gives the detailed pattern of diffuse scattering of the high temperature phase of $KTiF_4$ by means of an electron microscope.

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ΠΕΡΙΛΗΨΗ

ΔΟΜΙΚΕΣ ΑΛΛΑΓΕΣ ΦΑΣΗΣ ΣΤΟ $KTiF_4$

Υπό

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Σε μονοκρυστάλλους $KTiF_4$ παρατηρήθηκαν μετατροπές φάσης με αλλαγή της θερμοκρασίας στο ηλεκτρονικό μικροσκόπιο. Οι μετατροπές αυτές φάσης μπορεί να αποδοθούν σε περιστροφικές κινήσεις των οκταέδρων TiF_4 γύρω από τους κύριους άξονές τους. Με τον τρόπο αυτό μπορεί να αλλάξει η περιοδικότητα της δομής και να προκύψει κυψελίδα πολλαπλάσια της αρχικής κυψελίδας της ιδανικής φάσης όπου τα οκτάεδρα δεν έχουν περιστροφές γύρω από τους άξονές τους. Εκτός των αλλαγών περιοδικότητας της δομής παρατηρήθηκαν και περιοδικές γραμμές διάχυτης ακτινοβολίας που οφείλονται σε κατάσταση περιορισμένης τάξης στη φάση των περιστροφικών κινήσεων των οκταέδρων κατά μήκος των κύριων αξόνων τους.