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Evidence of the orthorhombic D_{2h}^{18} symmetry of K_2CuF_4: Phonon-Raman scattering measurements

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We report phonon-Raman spectra observed in a crystal of K_2CuF_4 that is made up entirely of single-domain structure. Among the 18 Stokes lines expected from the group-theoretical analysis of the space group of D_{2h}^{18}, the space group of K_2CuF_4 proposed by Hidaka and Walker, 17 lines are observed and 1 line is missing. Each observed line is successfully assigned to the irreducible representation of the D_{2h} point group, so that its orthorhombic crystal symmetry is confirmed. This is the first report of an experiment on a single-domain crystal of K_2CuF_4. The spectra of a multidomain crystal structure, on the other hand, are found to have more or less traces of the orthorhombic symmetry. We point out, therefore, that it is inadequate to treat such a crystal in the category of tetragonal symmetry, as employed to date in many studies on this compound.

I. INTRODUCTION

The layer compound K_2CuF_4 has been playing an important role in the investigation of two-dimensional ferromagnetism. Besides its magnetic properties this compound has an attractive aspect in its structure itself. Due to the Jahn-Teller effect in Cu^{2+}, CuF_6 octahedra are elongated along one of the respective principal axes and are arranged cooperatively with their longest axes orthogonal to each other in the c plane. This two-dimensional "antiferrodistortive" order was established both experimentally and theoretically in an early stage of the development of research for this compound. For a crystal structure of K_2CuF_4, however, several different models have been proposed as reviewed in Ref. 1.

Among them, a model given by Hidaka and Walker[1] is now recognized as a correct one. We think that the ambiguities of its crystal structure arise from both the ways of stacking the c planes[2] and the formation of domains.[3] According to the report by Itoh and Akimitsu,[3] there are two types of domain. When a crystal consists of one type of domain, it has a twofold symmetry around the c axis, while in a crystal having coexistence of two types of domain, i.e., in a multidomain crystal, the c axis looks similar to a fourfold symmetric axis.

Hidaka and Walker[1] have made clear these circumstances and have expressed that a single-domain crystal has the orthorhombic D_{2h}^{18} symmetry with the unit cell of $\sqrt{2}a_p \times \sqrt{2}b_p \times c_p$ ($a_p = b_p$), where $a_p \times a_p \times c_p$ is the unit cell of a K_2NiF_4-type structure (see Fig. 1). Though an orthorhombic symmetry usually indicates $a_p \neq b_p$, in the present case, however, the twofold symmetry comes only from the stacking condition of the c planes, so that it neither means an orthorhombic distortion nor the relation of $a_p \neq b_p$.

There have appeared several reports even after the paper of Ref. 1 in which respective experimental results are analyzed on the basis of wrong models of the structure.[4] Such wrong views concerning its structure, are, in our

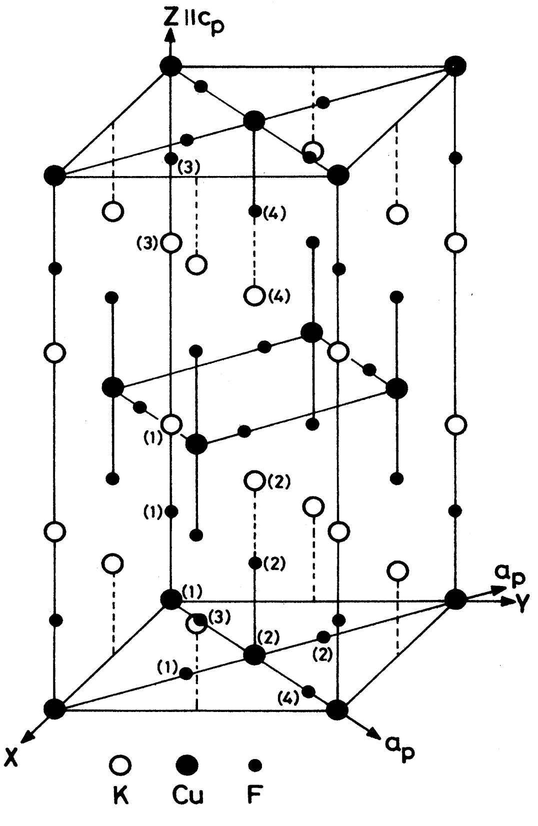

FIG. 1. Unit cell of K_2CuF_4 with a single-domain structure. The position of each inequivalent atom is given in the coordinate system $[X,Y,Z]$ as follows: Cu(1)[000], Cu(2)$[\frac{1}{2}\frac{1}{2}0]$, $F^a(1)[\frac{1}{2}+x\,\frac{1}{2}-x\,0]$, $F^a(2)[\frac{1}{2}-x\,\frac{1}{2}+x\,0]$, $F^a(3)[+x\,+x\,0]$, $F^a(4)[-x\,-x\,0]$, $F^c(1)[00+u']$, $F^c(2)[\frac{1}{2}\frac{1}{2}+u']$, $F^c(3)[00-u']$, $F^c(4)[\frac{1}{2}\frac{1}{2}-u']$, K(1)$[00u]$, K(2)$[\frac{1}{2}\frac{1}{2}+u]$, K(3)$[00-u]$, K(4)$[\frac{1}{2}\frac{1}{2}-u]$, where F^a and F^c indicate the F atoms in the c plane and on the c axis, respectively.

opinion, solely attributed to the lack of careful examination of the quality or the result of crystallization of the samples employed. As reported earlier,[2] a crystal grown as K_2CuF_4 scarcely shows its genuine structure and most of them contain parts of stacking disorders of the *c* planes along the *c* axis. Even in a crystal having a perfect stacking order, mixing of the two different types of domain is usually unavoidable.

In such multidomain samples, the approximate tetragonal D_{4h}^{5} symmetry has been used.[5-7] Kaneko *et al.*[5] made the experimental study of phonon-Raman scattering on K_2CuF_4 and explained the result on the assumption of the space group of D_{4h}^{5}. At that time (before the paper of Ref. 1), the crystal structure was not known precisely, so that they did not examine the samples from the point of view of the domain structures. To get intrinsic phenomena of K_2CuF_4, especially in neutron, x-ray, or optical scattering experiments, we must use a single-domain crystal without stacking irregularity.

Amongst many crystals grown by ourselves, we found one having a single-domain part large enough for optical measurements. Cutting out this part we have made experiments of phonon-Raman scattering on it and have obtained perfect spectra expected from the space group of D_{2h}^{18}. In the present paper we shall represent phonon-Raman spectra of K_2CuF_4 with a perfect single-domain structure and assign each observed Stokes line to the irreducible representation expected from the space group of D_{2h}^{18}. To compare with the result of a single-domain sample we shall also show spectra obtained in a multidomain sample.

In Sec. II we shall briefly review the crystal structure reported by Hidaka and Walker. The result of the group analysis and the experimental procedure will be given in Secs. III and IV, successively. Finally, we shall show experimental spectra and give a discussion in Sec. V. As a result of the present study, we intend to establish the correct crystal structure of K_2CuF_4.

II. CRYSTALLOGRAPHY OF K_2CuF_4

Since the reason why the space group of the single-domain crystal should be D_{2h}^{18} is explained in Ref. 1, in this section we shall give a brief review of it. As expected from its structure the bonding between adjacent *c* planes is very weak so that there arise two ways of stacking the *c* planes along the *c* axis, which results in the formation of two types of domain structure as schematically shown in Fig. 2. In the following discussion we take *X*, *Y*, and *Z* for the laboratory axes as shown in Fig. 1; *Z* is parallel to the *c* axis, whereas *X* is parallel to one of the $[110]_p$ axes and *Y* is perpendicular to *X* in the *c* plane where $[\ ]_p$ indicates an axis in the unit cell of a K_2NiF_4-type structure. The two types are essentially identical to each other because one becomes the other by rotating itself through 90° around the *c* axis. Since a multidomain sample has a mixing of both, it then becomes impossible to distinguish *X* from *Y*. As a consequence the sample seems as if it has a fourfold axial symmetry.

In the unit cell $\sqrt{2}a_p \times \sqrt{2}a_p \times c_p$ which contains two molecules there are 14 atoms for which symmetry operations should be made in the factor-group analysis. To show the inequivalence of sites, we put a number to each atom similar to Cu(1), Cu(2), F(1), F(2), . . . as explained in Fig. 1. Furthermore we distinguish the F atoms on the *c* axis from those in the *c* plane by F^c and F^a. From now on we will call the sample with a single-domain and multidomain structure *s*-K_2CuF_4 and *m*-K_2CuF_4, respectively.

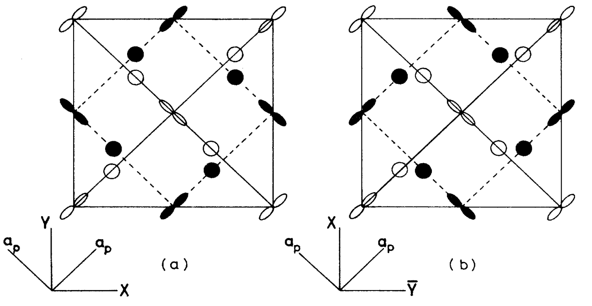

FIG. 2. Domain patterns projected on the *c* planes. F atoms (circles) displaced from the midpoint of Cu—Cu bondings and the hole orbitals of Cu^{2+} are shown. Black ones are those in one of the nearest-neighbor *c* planes containing Cu atoms. The *X* axis is parallel to one of the $[110]_p$ directions and *Y* is perpendicular to *X* where $[\ ]_p$ indicates a direction in the unit cell of a K_2NiF_4-type structure. When the axes *X* and *Y* are exchanged, type (a) becomes (b) and vice versa.

III. FACTOR-GROUP ANALYSIS

Here we represent the result of the factor-group analysis for the space group of D_{2h}^{18}. Since the unit cell has 14 atoms then 42 normal modes are expected. Based on a standard method of the factor-group analysis, we obtain the irreducible representations expressed following the notation for the point group of D_{2h} as

$$\Gamma(D_{2h}^{18})=4A_g+4B_{1g}+5B_{2g}+5B_{3g}+4A_u$$
$$+4B_{1u}+8B_{2u}+8B_{3u} \; .$$

Among them, the Raman-active modes are given as

$$\Gamma=4A_g+4B_{1g}+5B_{2g}+5B_{3g} \; .$$

Then 18 Stokes lines are expected.

The nonzero components of the Raman tensors of D_{2h} are given as follows:

$$A_g:\ \alpha_{XX},\ \alpha_{YY},\ \alpha_{ZZ} \; ,$$
$$B_{1g}:\ \alpha_{XY} \; ,$$
$$B_{2g}:\ \alpha_{XZ} \; ,$$
$$B_{3g}:\ \alpha_{YZ} \; .$$

From these components, the Stokes lines should be produced for the configurations of polarization directions of the incident and scattered light as follows:

four lines of the A_g modes in XX, YY, or ZZ,
four lines of the B_{1g} modes in XY,
five lines of the B_{2g} modes in XZ,
five lines of the B_{3g} modes in YZ polarization.

IV. EXPERIMENTAL PROCEDURE

The single-domain part was cut out and shaped into a rectangular parallelepiped of 2×2×1 mm^3 size (1 mm thick along the c axis) with the faces of $(001)_p$, $(110)_p$, and their equivalences. Each face was polished up to an unevenness of about 1 μm.

We used a Raman spectrometer set up by ourselves consisting of a double monochromator (CT-1000D, Jasco) and a photon counter (C-767, Hamamatsu) with a cooled photomultiplier (R-943-02, Hamamatsu), besides several optical elements such as mirrors, prisms, lenses, etc. A 514.5-nm polarized line of an argon laser was employed as a light source and all spectra were collected in a microcomputer. The polarization of the scattered light was analyzed with Polaroid HN-38 film. A quartz wedge, placed just in front of the entrance slit of the monochromator, was used to depolarize the scattered light.

The sample was inserted into a liquid helium cryostat designed by us. To get low temperatures, liquid helium was drawn from the main reservoir through a needle valve. In the combination of adjusting the valve with the automatically controlled power of the heater attached to a sample holder, the temperature was kept constant during the scanning of the wave numbers. Employing 90° scattering geometry we obtained Raman spectra in XX, ZZ, XY, XZ, and YZ polarizations.

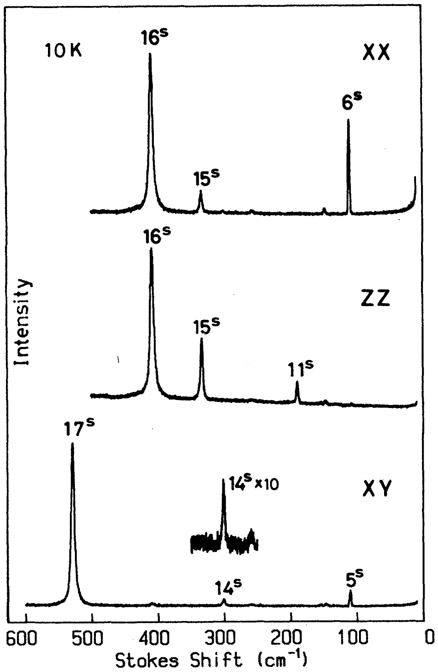

FIG. 3. Polarized phonon-Raman spectra of K_2CuF_4 with a single-domain structure observed at 10 K.

V. EXPERIMENTAL RESULTS AND DISCUSSION

A. Single-domain sample

We show in Figs. 3 and 4 the Raman spectra observed at 10 K for each configuration of polarization. For the convenience of discussion, we assign a number to each line such as 1^s, 2^s, 3^s, . . . , 17^s according to the value of the Stokes shift. The doubly numbered line 8^s+9^s consists of two different modes, which will be clarified later.

Several lines observed in the XZ and YZ spectra are shown in Fig. 5 on the expanded scales of the wave numbers. The difference of the XZ from YZ spectrum indicates characteristics of the single-domain structure, i.e., a twofold symmetry of the crystal or $X \neq Y$.

As explained above, the Stokes lines corresponding to the normal modes represented as A_g are expected to appear in the XX, YY, or ZZ spectrum. We find in Fig. 3 three lines in the XX spectrum, i.e., 6^s (110.5 cm^{-1}), 15^s (333.5 cm^{-1}), and 16^s (408.6 cm^{-1}), and also three lines in the ZZ spectrum, i.e., 11^s (189.4 cm^{-1}), 15^s (333.5 cm^{-1}), and 16^s (408.6 cm^{-1}). As a result all four lines of the A_g modes are confirmed.

Four Stokes lines corresponding to the modes represented as B_{1g} are expected to appear only in the spectrum of the XY polarization. The XY spectrum in Fig. 3 shows three lines, 5^s (110.1 cm^{-1}), 14^s (301.2 cm^{-1}), and 17^s (528.8 cm^{-1}), that are inevitably of the B_{1g} mode, so that one line is missing. We withhold, at present, referring to the reason why one line is absent in the XY spectrum because it requires a quantitative analysis concerning the scattering intensity that is irrelevant to the present purpose.

In the XZ and YZ spectra, on the other hand, four peaks (1^s, 3^s, 8^s+9^s, and 12^s) and five peaks (2^s, 4^s, 7^s, 10^s, and 13^s) are observed, respectively. They should be of B_{2g} and B_{3g}, or vice versa. Since B_{2g} and B_{3g} are regard-

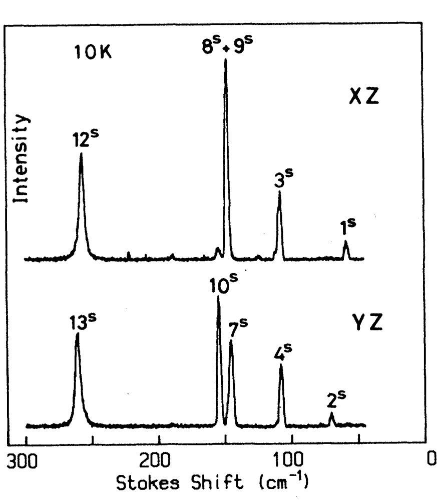

FIG. 4. XZ and YZ polarized phonon-Raman spectra of K_2CuF_4 with a single-domain structure observed at 10 K.

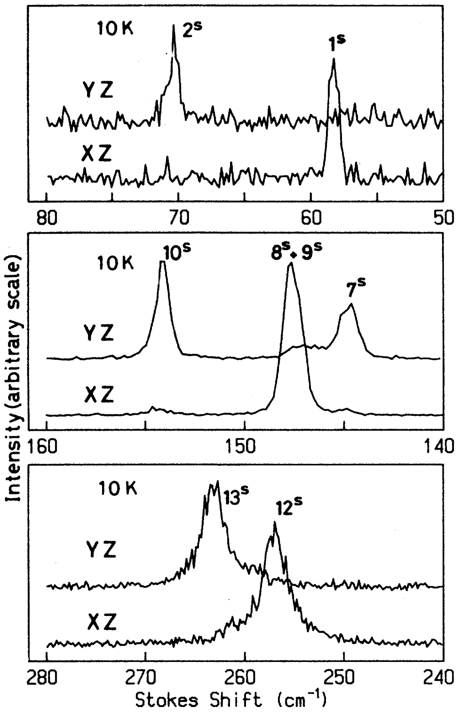

FIG. 5. Several lines in the *XZ* and *YZ* spectra of K_2CuF_4 with a single-domain structure. The difference between the *XZ* and *YZ* spectrum indicates the orthorhombic symmetry of the crystal.

TABLE I. List of the Stokes lines observed at 10 K in K_2CuF_4 with a single-domain structure and the assignment of the irreducible representation. For each line, the configuration of the polarization is attached.

No.	Energy (cm^{-1})	Polarization	Assignment D_{2h}^{18}
1^s	58.2	*XZ*	B_{2g}
2^s	70.1	*YZ*	B_{3g}
3^s	107.0	*XZ*	B_{2g}
4^s	107.0	*YZ*	B_{3g}
5^s	110.1	*XY*	B_{1g}
6^s	110.5	*XX*	A_g
7^s	144.7	*YZ*	B_{3g}
8^s	147.7	*XZ*	B_{2g}
9^s	147.7	*XZ*	B_{2g}
10^s	154.1	*YZ*	B_{3g}
11^s	189.4	*ZZ*	A_g
12^s	256.0	*XZ*	B_{2g}
13^s	263.2	*YZ*	B_{3g}
14^s	301.2	*XY*	B_{1g}
15^s	333.5	*XX* and *ZZ*	A_g
16^s	408.6	*XX* and *ZZ*	A_g
17^s	528.8	*XY*	B_{1g}
Missing line		*XY*	B_{1g}

ed as being due to the splitting of degenerate E_g modes when the symmetry is reduced from D_{4h} to D_{2h}, then each of the five lines observed in the *YZ* spectrum should have a counterpart in the *XZ* spectrum such as 2^s and 1^s, 4^s and 3^s, 13^s and 12^s, etc. The counterparts 3^s and 4^s appear at the same position indicating that the corresponding normal modes are insensitive to the exchange of *X* and *Y*. We think that the normal modes corresponding to these two lines are vibrations of K atoms along the *c* axis, i.e., the vibrations almost irrelevant to the cooperative distortion of CuF_6.

On the face of it, one line is absent in the *XZ* spectrum. When we compare the intensity ratio of the doubly numbered line 8^s+9^s to the line 3^s with that of 7^s to 4^s or 10^s to 4^s, however, we find that the intensity of the line 8^s+9^s is anomalously strong. Thus, it is natural to consider that the line 8^s+9^s consists of two lines 8^s and 9^s overlapping each other at the same position.

As explained above, we have received complete assignment of the 18 lines including one line missed in the *XY* spectrum that should correspond to one of the B_{1g} modes. All the Stokes lines observed and their respective irreducible representations are summarized in Table I. The present successful assignment is a perfect evidence of the orthorhombic symmetry of a genuine crystal of K_2CuF_4.

B. Multidomain sample

As explained above, two types of domain coexist in *m*-K_2CuF_4. In each domain, the orthogonal arrangement of the elongated CuF_6 octahedra in the *c* plane is correlated with those of the adjacent *c* planes, but the correlation is absent between the domains having different types. The population or the integrated thickness of the domains of respective types should vary from sample to sample.

Although the space group of D_{4h}^5 has been used for such a multidomain one, the present result shows that the characteristics of D_{2h}^{18} do not disappear completely. The *XY*, *XZ*, and *YZ* spectra observed in *m*-K_2CuF_4 show these circumstances. Since the *XX* and *ZZ* spectra of *m*-K_2CuF_4 were similar to those of *s*-K_2CuF_4, only the results obtained in *XY*, *XZ*, and *YZ* polarizations are shown in Fig. 6.

A very weak line denoted as (a) is observed in the *XY* spectrum at the position of line 5^s in *s*-K_2CuF_4, while the other two lines (b) and (c) correspond to 14^s and 17^s, respectively. One line is absent in this spectrum in the same way as *s*-K_2CuF_4. The factor-group analysis of D_{4h}^5 shows that one of the four normal modes of B_{1g} in D_{2h}^{18} is identical with the Raman-inactive mode A_{2g} in D_{4h}^5. We think, therefore, that the weak line (a) in the *XY* spectrum should completely disappear if the sample has the D_{4h}^5 symmetry. Thus the appearance of this line, although its intensity is very weak, indicates that the character of the twofold symmetry is still maintained.

In both *XZ* and *YZ* spectra, on the other hand, six lines numbered 1^m–6^m are observed. The positions of lines 1^m and 2^m correspond to those of 1^s and 2^s in *s*-K_2CuF_4 that appear separately in *XZ* and *YZ* spectra, re-

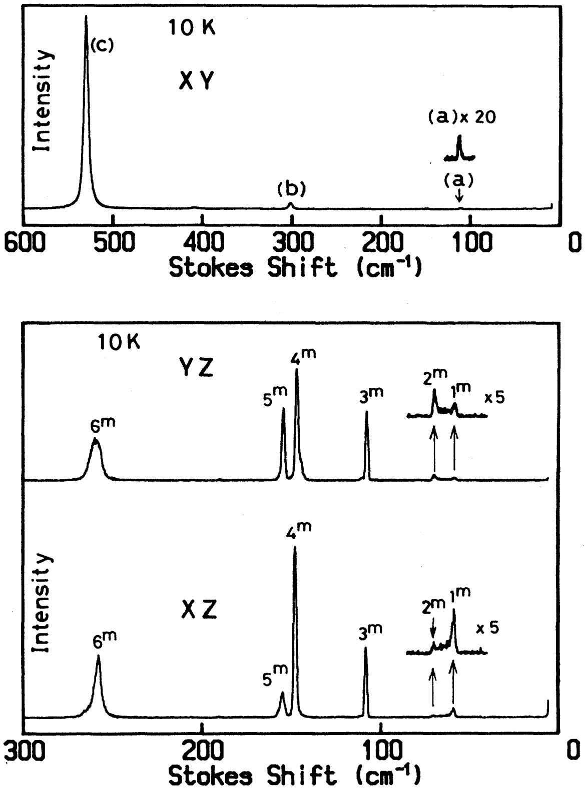

FIG. 6. Polarized phonon-Raman spectra of K_2CuF_4 with a multidomain structure observed at 10 K.

spectively, and the line 3^m is equivalent to 3^s. Over the range of 140–160 cm^{-1} there appear two lines at the same positions in both *XZ* and *YZ* spectra, though the relative intensities are different from each other. Furthermore, a broad line 6^m at 258.5 cm^{-1} also appears in both the *XZ* and *YZ* spectra.

If the sample with a multidomain structure is a complete system of D_{4h}^5, the counterparts assigned to the B_{2g} and B_{3g} modes for the D_{2h}^{18} symmetry should become a single line of the E_g mode for the D_{4h}^5 symmetry because the B_{2g} and B_{3g} modes are produced when the degeneracy of the E_g mode is removed as a result of the change from D_{2h}^{18} to D_{4h}^5.

The experimental *XZ* and *YZ* spectra, however, show pairs of peaks or broad lines at the positions corresponding to those of the lines observed in *s*-K_2CuF_4 independently in the *XZ* and *YZ* spectra and assigned to the B_{2g} or B_{3g} mode. For example, the lines denoted as 1^m and 2^m that appear in both *XZ* and *YZ* spectra correspond to 1^s and 2^s observed independently in the *XZ* and *YZ* spectra of *s*-K_2CuF_4. The appearance of these two lines in both *XZ* and *YZ* spectra is an evidence of the coexistence of the two types of domain both having larger thicknesses along the *c* axis than that of the wavelength of the incident light. For the same reason, the lines 4^m and 5^m that appeared in both *XZ* and *YZ* spectra correspond, respectively, to 8^s+9^s and 10^s in *s*-K_2CuF_4. Further, the line 6^m having a broad width or asymmetric shapes is considered as a result of the overlapping of the two lines corresponding to 12^s and 13^s. As mentioned above, the tetragonal D_{4h}^5 symmetry is inadequate for *m*-K_2CuF_4.

VI. CONCLUDING REMARKS

As we have discussed above, perfect Raman spectra of K_2CuF_4 with a single-domain structure were obtained. Each Stokes line is assigned to the irreducible representation of the D_{2h} point group. In the multidomain crystal, on the other hand, we find that the characters of the D_{2h}^{18} symmetry are more or less maintained. Our present results would be helpful to understand more exactly the Raman spectra of the isomorphous compound Rb_2CrCl_4.[8] Based on our present results, we insist on the importance of an examination of the crystals of K_2CuF_4, especially in x-ray, neutron, optical scattering experiments, etc. In such experiments, crystals having a stacking disorder should be avoided and their domain structures should be checked. If such strict examinations had been made, wrong models of its crystal structure, for example, the tetragonal D_{2d}^{10} symmetry proposed by Haegele and Babel,[9] would not have been reported. Here we emphasize that the crystals of K_2CuF_4 have occasionally stacking disorders and most of them have multidomain structures. Then it is basically inadequate to assign space groups to such multidomain crystals because they do not have periodicity in their structures. Instead, taking into account the population of the two types of domain one should employ the D_{2h}^{18} symmetry even for multidomain ones.

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