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LATTICE DYNAMICS OF CRYSTALS HAVING
RUTILE STRUCTURE

(FeF_2 , MnF_2 , MgF_2 and TiO_2)

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ABSTRACT

Using Born's theory the secular equation has been formulated for the dynamics of the rutile structure. Group theoretical method has been used to decompose it into smaller degree equations at the centre of the Brillouin zone. On account of the electrostatic contribution to the elements of the secular equation, these elements do not have unique values at the wave vector $q=0$, but rather depend on the direction in which the wave vector tends to zero. In order to get the expressions for all the infrared active transverse and longitudinal modes, it is necessary to make the calculations for the wave vector $\rightarrow 0$ along the two non-equivalent crystallographic axes of the rutile structure. The frequencies of vibration of iron fluoride, Manganese fluoride, magnesium fluoride and rutile have been calculated using rigid ion model with short range axially symmetric forces and long range Coulomb forces.

1. INTRODUCTION

Recently for the interpretation of the Raman and infrared spectra of rutile, a group theoretical analysis of the vibration spectrum at zero wave vector was carried out by Cubanov and Shur¹. Some of the symmetry relations, however, used by them appear to be incorrect. The formulae for the frequencies of the various modes of the rutile structure² as $q \rightarrow 0$ have been

rederived by us and have been successfully applied for evaluating the vibration frequencies of the fluorides of iron, manganese and magnesium and titanium oxide. The results are presented here.

2. THEORETICAL DERIVATION OF FORMULAE FOR FREQUENCIES

The unit cell of rutile lattice may be taken as shown in Fig. 1, consisting of $2 Ti^{4+}$ and $4 O^{2-}$ ions distinguished by the indices $k=1, 2 \dots 6$ as indicated. The vibration frequencies are obtained as the solutions of the secular equation²,

$$\left| \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} - \omega^2 \delta_{kk'} \delta_{\alpha\beta} \Big| = 0 \quad [1]$$

where

$$\left\{ \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} = \frac{1}{(m_k m_{k'})^{1/2}} \left[\begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right] \quad [2]$$

The symbols have their usual meaning³. On account of the ionic forces in the lattice, the coefficients $\left[\begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right]$ will not have unique value at the centre of the Brillouin zone but depend on the direction in which the wave vector q approaches zero and since the two directions, namely a_2 and a_3 , are non-equivalent, the symmetry relations existing between the coupling coefficients $\left[\begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right]$ at $q=0$ are not same for these two directions.

The symmetry relations between the quantities $\left[\begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right]$ following from the symmetry of rutile structure for $q \rightarrow 0$ in the direction a_2 are given in Table 1. For the wave vector $q \rightarrow 0$ in the direction a_3 , these relations can be obtained from the Table 1 by making use of the following equalities.

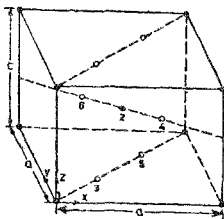


FIG. 1

The Unit Cell of Rutile Lattice.

TABLE I

Symmetry relations between the coupling coefficients for the limit $q \rightarrow 0$ along a_z direction

| KK' | xx | yy | zz | xy | yz | zx |
|-------|----------|----------|----------|-----------|------|------|
| 11 | a_{xx} | a_{xx} | a_{zz} | a_{xy} | 0 | 0 |
| 12 | b_{xy} | b_{yy} | b_{zz} | 0 | 0 | 0 |
| 13 | c_{xz} | c_{yy} | c_{zz} | c_{xy} | 0 | 0 |
| 14 | d_{xx} | d_{yy} | d_{zz} | d_{xy} | 0 | 0 |
| 15 | e_{xx} | e_{yy} | e_{zz} | e_{xy} | 0 | 0 |
| 16 | a_{xy} | d_{yy} | d_{zz} | d_{xy} | 0 | 0 |
| 22 | a_{xy} | a_{xx} | a_{zz} | $-a_{xy}$ | 0 | 0 |
| 23 | d_{xy} | d_{yy} | d_{zz} | $-d_{xy}$ | 0 | 0 |
| 24 | e_{xy} | e_{yy} | e_{zz} | $-e_{xy}$ | 0 | 0 |
| 25 | d_{xy} | d_{yy} | d_{zz} | $-d_{xy}$ | 0 | 0 |
| 26 | e_{xy} | e_{yy} | e_{zz} | $-e_{xy}$ | 0 | 0 |
| 33 | e_{xy} | e_{xx} | e_{zz} | e_{xy} | 0 | 0 |
| 34 | f_{xy} | f_{yy} | f_{zz} | 0 | 0 | 0 |
| 35 | g_{xy} | g_{yy} | g_{zz} | g_{xy} | 0 | 0 |
| 36 | h_{xx} | h_{yy} | f_{zz} | 0 | 0 | 0 |
| 44 | e_{xx} | e_{xx} | e_{zz} | $-e_{xy}$ | 0 | 0 |
| 45 | h_{xx} | h_{yy} | f_{zz} | 0 | 0 | 0 |
| 46 | g_{xx} | g_{yy} | g_{zz} | $-g_{xy}$ | 0 | 0 |
| 55 | e_{xy} | e_{xy} | e_{zz} | e_{xy} | 0 | 0 |
| 56 | f_{xx} | f_{yy} | f_{zz} | 0 | 0 | 0 |
| 66 | e_{xx} | e_{xx} | e_{zz} | $-e_{xy}$ | 0 | 0 |

$$b_{xx} = b_{yy}, \quad c_{xx} = c_{yy}, \quad d_{xx} = d_{yy} \quad [3]$$

$$g_{xx} = g_{yy}, \quad f_{xx} = h_{yy} \quad \text{and} \quad f_{yy} = h_{xx} \quad [4]$$

In order to factorise the secular determinant into smaller degree equations we have to find the unitary matrix U such that $\tilde{U} \begin{Bmatrix} k & k' \\ \alpha & \beta \end{Bmatrix} U$ is reduced to diagonal form. This matrix can be obtained with the help of the symmetry coordinates for the structure. The latter are obtained with the help of the following relation.

$$\psi^i = \sum_R X_i(R) R q_\alpha \quad [5]$$

where, ϕ^i is a symmetry coordinate corresponding to the i th irreducible representation, $\chi_i(R)$ is the character under the operation R and q_α is the mass weighted displacement vector of the ion in the direction α ; ($\alpha = x, y, z$). In case where more than one normal mode belong to the same irreducible representation, the vectors ϕ^i obtained may not be linearly independent, However, using Schmidts process of orthogonalization they can be made linearly independent. The unitary matrix can now be obtained using the relation,

$$U_{ij} q_j = \phi_i^j \quad [6]$$

The matrix U thus obtained is given in Table 2 in the following form

$$U = U^0 N \quad [7]$$

where N is a diagonal matrix.

$$N_{ij, i'j'} = N_{ij} \delta_{ii'} \delta_{jj'} \quad [8]$$

and it takes into account the normalisation of the basic vectors.

Carrying out the transformation of the matrix $\begin{Bmatrix} k & k' \\ \alpha & \beta \end{Bmatrix}$ with the matrix U obtained above, one obtains as expected, a matrix which is diagonal except for the irreducible representations to which more than one normal mode belong. The frequency expressions thus obtained for wave vector $q \rightarrow 0$ along z_2 are given below:

$$\left. \begin{aligned} A_{1g} : m_2 \omega_1^2 &= e_{xx} + f_{xx} - g_{xx} - h_{xx} + e_{xy} - g_{xy} \\ A_{2g} : m_2 \omega_2^2 &= e_{xx} - f_{xx} - g_{xx} + h_{xx} - e_{xy} + g_{xy} \\ B_{1g} : m_2 \omega_3^2 &= e_{xx} + f_{xx} - g_{xx} - h_{xx} - e_{xy} + g_{xy} \\ B_{2g} : m_2 \omega_4^2 &= e_{xx} - f_{xx} - g_{xx} + h_{xx} + e_{xy} - g_{xy} \\ E_g : m_2 \omega_5^2 &= e_{zz} - g_{zz} \\ A_{2u} : \omega_6^2 \text{ (T.O.)} &= [(m_1 + 2m_2)/2m_1 m_2] (a_{zz} + b_{zz}) \\ \omega_7^2 \text{ (L.A.)} &= 0 \end{aligned} \right\} [9]$$

$B_{1u} : \omega_8$ and ω_9

$$\left\{ \begin{array}{ll} (1/m_1) (e_{zz} - 2f_{zz} + g_{zz}) - \omega^2 & (2/m_1 m_2)^{1/2} (c_{zz} - d_{zz}) \\ (2/m_1 m_2)^{1/2} (c_{zz} - d_{zz}) & (1/m_1) (a_{zz} - b_{zz}) - \omega^2 \end{array} \right\} = 0$$

$$E_n: \omega_{10}^2 (\text{T.A.}) = 0$$

$$\omega_{11} (\text{T.O.}), \omega_{11} (\text{L.O.}), \omega_{12} (\text{T.O.}), \omega_{12} (\text{L.O.}), \omega_{13} (\text{T.O.}), \omega_{13} (\text{L.O.})$$

$$\left[\begin{array}{cccccc} A_{11} - \omega^2 & A_{12} & A_{13} & A_{14} & A_{15} & A_{16} \\ & A_{22} - \omega^2 & A_{23} & A_{24} & A_{25} & A_{26} \\ & & A_{33} - \omega^2 & A_{34} & A_{35} & A_{36} \\ & & & A_{44} - \omega^2 & A_{45} & A_{46} \\ & & & & A_{55} - \omega^2 & A_{56} \\ & & & & & A_{66} - \omega^2 \end{array} \right] = 0$$

(symmetric part)

[10]

$$\text{where } A_{11} = A_{44} = (1/2m_1) (2a_{xx} - b_{xx} - b_{yy})$$

$$A_{12} = A_{45} = (1/2m_1 m_2)^{1/2} (c_{xx} - d_{xx} + c_{yy} - d_{yy})$$

$$A_{13} = A_{46} = (2/m_1) [(m_1 + 2m_2/2m_2)]^{1/2} (e_{xy} + d_{xy})$$

$$A_{14} = (1/2m_1) (b_{yy} - b_{xx})$$

$$A_{15} = (1/2 m_1 m_2)^{1/2} (c_{xx} - d_{xx} - c_{yy} + d_{yy})$$

$$A_{16} = (A_{26} = A_{34} = A_{35} = 0)$$

$$A_{22} = A_{55} = (1/2m_2) (2e_{xx} - f_{xx} + g_{xx} - h_{xx} - f_{yy} + g_{yy} - h_{yy})$$

$$A_{23} = A_{56} = (1/m_2) [(m_1 + 2m_2)/m_1]^{1/2} (d_{xy} - c_{xy})$$

$$A_{24} = (1/2 m_1 m_2)^{1/2} (c_{xx} - d_{xx} - c_{yy} + d_{yy})$$

$$A_{25} = (1/2m_2) (f_{yy} - g_{yy} + h_{yy} - f_{xx} + g_{xx} - h_{xx})$$

$$A_{33} = A_{66} = [(m_1 + 2m_2)/4m_1 m_2] (2a_{xx} + b_{xx} + b_{yy})$$

$$A_{36} = [(m_1 + 2m_2)/4m_1 m_2] (h_{yy} - b_{xx})$$

where m_1 and m_2 are the masses of titanium and oxygen atoms respectively. We notice that due to the presence of the macroscopic field the degenerate infrared active modes split up into corresponding transverse and longitudinal vibrations for the wavevector $q \rightarrow 0$ along \mathbf{a}_2 and since the atomic motions in the A_{2u} mode are confined to the z direction, we get an expression for the transverse frequency when the limit $q \rightarrow 0$ is taken in the direction \mathbf{a}_2 . The Raman active mode E_g , however, remains degenerate as the motions of the anions in opposite directions does not produce any change in the macroscopic dielectric polarisations. The atomic motions of E_u modes are confined to the xy -plane and therefore for a wavevector $q \rightarrow 0$ along \mathbf{a}_3 the normal modes corresponding

TABLE
Transformation

| $\alpha_h \setminus ij$ | E_{2u}^0 | A_{2u}^0 | $E_u^1(a)$ | $E_u^2(a)$ | $E_u^3(a)$ | $E_u^1(b)$ | |
|-------------------------|--|----------------|--|------------|--|-----------------|----|
| x_1 | $1/\sqrt{m_2}$ | 0 | 0 | 1 | 0 | $-2/\sqrt{m_1}$ | 1 |
| x_2 | $1/\sqrt{m_2}$ | 0 | 0 | -1 | 0 | $-2/\sqrt{m_1}$ | -1 |
| y_1 | 0 | $1/\sqrt{m_2}$ | 0 | 1 | 0 | $-2/\sqrt{m_1}$ | -1 |
| y_2 | 0 | $1/\sqrt{m_2}$ | 0 | -1 | 0 | $-2/\sqrt{m_1}$ | 0 |
| z_1 | 0 | 0 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 |
| z_2 | 0 | 0 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 |
| x_3 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 1 | $1/\sqrt{m_2}$ | 0 |
| x_4 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | -1 | $1/\sqrt{m_2}$ | 0 |
| x_5 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 1 | $1/\sqrt{m_2}$ | 0 |
| x_6 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | -1 | $1/\sqrt{m_2}$ | 0 |
| y_3 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 1 | $1/\sqrt{m_2}$ | 0 |
| y_4 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | -1 | $1/\sqrt{m_2}$ | 0 |
| y_5 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 1 | $1/\sqrt{m_2}$ | 0 |
| y_6 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | -1 | $1/\sqrt{m_2}$ | 0 |
| z_3 | 0 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 0 |
| z_4 | 0 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 0 |
| z_5 | 0 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 0 |
| z_6 | 0 | 0 | $1/\sqrt{m_1}$ | 0 | 0 | 0 | 0 |
| ij | E_u^0 | A_{2u}^0 | $E_u^3(a)$ | $E_u^3(b)$ | A_{2u} | | |
| N_{ij} | $\left[\frac{m_1 m_2}{2(m_1 + 2m_2)} \right]^{1,2}$ | | $\left[\frac{m_1 m_2}{8(m_1 + 2m_2)} \right]^{1,2}$ | | $\left[\frac{m_1 m_2}{4(m_1 + 2m_2)} \right]^{1,2}$ | | |

Matrix U

| $E_u^2(b)$ | $E_u^3(b)$ | B_{1u}^1 | B_{1u}^2 | A_{2u} | A_{1g} | A_{2g} | B_{1g} | B_{2g} | $E_g(a)$ | $E_g(b)$ |
|---------------|-----------------|------------|------------|----------------------|----------|--|----------|----------|----------|----------|
| 0 | $2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | $2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | $-2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | $-2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 1 | 0 | $2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | -1 | 0 | $2/\sqrt{m_1}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 0 | 0 |
| -1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 1 | -1 | 1 | -1 | 0 | 0 |
| 1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | -1 | -1 | -1 | -1 | 0 | 0 |
| -1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | -1 | 1 | -1 | 1 | 0 | 0 |
| -1 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | 1 | -1 | -1 | 1 | 0 | 0 |
| 1 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | -1 | -1 | 1 | 1 | 0 | 0 |
| -1 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | -1 | 1 | 1 | -1 | 0 | 0 |
| 1 | $1/\sqrt{m_2}$ | 0 | 0 | 0 | 1 | 1 | -1 | -1 | 0 | 0 |
| 0 | 0 | 0 | 1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 | 1 | 0 |
| 0 | 0 | 0 | -1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 | 0 | 1 |
| 0 | 0 | 0 | 1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 | -1 | 0 |
| 0 | 0 | 0 | -1 | $-1/\sqrt{m_2}$ | 0 | 0 | 0 | 0 | 0 | -1 |
| $E_u^1(a)$ | $E_u^1(b)$ | B_{1u}^2 | B_{1u}^1 | $E_g(a)$ | $E_g(b)$ | $E_u^2(a), E_u^2(b), A_{1g}, A_{2g}, B_{1g}, B_{2g}$ | | | | |
| $\frac{1}{2}$ | | | | $\sqrt{\frac{1}{2}}$ | | $\sqrt{\frac{1}{8}}$ | | | | |

to E_u representation are purely transverse and the degeneracies are not removed. The frequency expression A_{2u} mode will yield the corresponding longitudinal frequency for this direction. The modified formulae for the infrared active vibrations for the wave vector $q \rightarrow 0$ along a_3 are given below :

$$A_{2u} : \omega_2^2 (\text{L.O.}) = [(m_1 + 2m_2)/2m_1m_2] (a_{zz} + b'_{zz})$$

$$E_u : \omega_{11} (\text{T.O.}), \omega_{12} (\text{T.O.}), \omega_{13} (\text{T.O.})$$

$$\begin{vmatrix} A_{11} - \omega^2 & A_{12} & A_{13} \\ A_{12} & A_{22} & A_{23} \\ A_{13} & A_{23} & A_{33} - \omega^2 \end{vmatrix} = 0$$

where

$$A_{11} = (1/m_1) (a_{xx} - b_{xx})$$

$$A_{12} = (2/m_1 m_2)^{1/2} (c_{xx} - d_{xx})$$

$$A_{13} = (2/m_1) [(m_1 + 2m_2)/2m_2]^{1/2} (c_{xy} + d_{xy})$$

$$A_{22} = (1/m_2) (e_{xx} - f_{xx} + g_{xx} - h_{xx})$$

$$A_{23} = (1/m_2) [(m_1 + 2m_2)/m_1] (d_{xy} - c_{xy})$$

$$A_{33} = [(m_1 + 2m_2)/2m_1 m_2] (a_{xx} + b_{xx}).$$

The frequency expressions for the normal modes belonging to the other irreducible representations are, however, the same as for $q \rightarrow 0$ along a_2 . It may be noticed that these formulae for normal modes are different from those derived by Gubanov and Shur¹. They took the coefficients $\begin{bmatrix} k & k \\ x & y \end{bmatrix}$ as equal to zero. We do not find any justification for equating these coefficients to zero as the symmetry of the structure does not impose any such condition. Consequently their short range forces are charge dependent [Eq. 10 of ref. 1] and vanish when the effective charges on the ions are zero. Secondly, their formulae do not account for the electrostatic splitting of the infrared active modes.

For the calculation of the vibration frequencies of the crystals having rutile structure, the long range Coulomb forces of attraction between point ions and the repulsive forces between neighbouring ions were considered. The short range potential function was assumed to be axially symmetric and the corresponding coupling coefficients $\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}$ are given in reference 3. The electrostatic co-efficients $c_{\alpha\beta} \begin{pmatrix} 0 \\ k & k' \end{pmatrix}$ for various crystals having rutile structure

are given in Table 3 and these can be used to obtain the Coulomb part of the coupling coefficients $\begin{bmatrix} k k' \\ \alpha \beta \end{bmatrix}$ with the help of the following equation :

$$\begin{bmatrix} k k' \\ \alpha \beta \end{bmatrix} = \frac{e^2}{v} z_k c_{\alpha\beta} \begin{pmatrix} 0 \\ k k' \end{pmatrix} z_{k'} - \delta_{kk'} \sum_{k''} z_k c_{\alpha\beta} \begin{pmatrix} 0 \\ k k'' \end{pmatrix} z_{k''}$$

The structural parameters used in the calculation of these coefficients are those reported by Bau⁴ and are given below :

| | <i>a</i> | <i>c</i> | <i>u</i> |
|--------------------|----------|----------|----------|
| Ironfluoride | 4.6960 Å | 3.3090 Å | 0.300 |
| Manganese fluoride | 4.8734 Å | 3.3699 Å | 0.305 |
| Magnesium fluoride | 4.6210 Å | 3.0500 Å | 0.303 |
| Rutile | 4.5929 Å | 2.9591 Å | 0.306 |

It is to be mentioned that in the earlier calculations on magnesium fluoride^{3,5} and rutile⁶ the value of *u* used was 0.31 as reported by Wyckoff⁷ and therefore it was found necessary to repeat those calculations using the values of *u* as reported above.

The elements of the dynamical matrix can now be written as

$$\begin{bmatrix} k k' \\ \alpha \beta \end{bmatrix} = \begin{bmatrix} k k' \\ \alpha \beta \end{bmatrix} + \begin{bmatrix} k k' \\ \alpha \beta \end{bmatrix}$$

In order to estimate the values of the short range parameters and the effective charge on the ions, a least square analysis was carried out so as to give the best fit to the observed Raman and infrared frequencies. The parameters thus obtained are given in Table 4 and the calculated and observed frequencies are listed Table 5. The observed Raman frequencies are those given by Porto⁸ *et al.* and the infrared frequencies by Barke⁹, Eagels¹⁰, Parisot¹¹ and Balkanski *et al.*¹² A comparison of the calculated and observed frequencies in these crystals shows a very good agreement between the two except for A_{2u} transverse optical mode, especially in rutile. This discrepancy is probably due to the neglect of the polarisation forces in these crystals and therefore a model which takes account of these forces should give a better fit to the experimental values.

TABLE 3
Coulomb coefficients $C_{\alpha\beta}(\frac{q}{hkl})$ for crystals having rutile structure

| q | kk' | Iron fluoride | Manganese fluoride | Magnesium fluoride | Rutile | |
|--|-------|---------------|--------------------|--------------------|-----------|-----------|
| $q_x = q_z = 0$ $q_y \rightarrow 0$ | kk | xx | -1.47736 | -1.09860 | -0.78631 | -0.50925 |
| | | yy | 11.08902 | 11.46777 | 11.78006 | 12.05713 |
| | | zz | -9.61166 | -10.36917 | -10.99375 | -11.54788 |
| | | xy | 0.0 | 0.0 | 0.0 | 0.0 |
| 12 | xx | xx | -5.71644 | -5.80961 | -5.87335 | -5.92286 |
| | | yy | 6.84993 | 6.75678 | 6.69252 | 6.64352 |
| | | zz | -1.13351 | -0.94717 | -0.81867 | -0.72066 |
| 13 | xx | xx | -8.88108 | -8.47108 | -8.35385 | -8.12685 |
| | | yy | 3.68528 | 4.09529 | 4.21252 | 4.43952 |
| | | zz | 5.19580 | 4.37579 | 4.14133 | 3.68733 |
| | | xy | -11.69711 | -10.61803 | -10.64718 | -10.04218 |
| 14 | xx | xx | 1.53159 | 1.86800 | 1.53006 | 1.71759 |
| | | yy | 14.09796 | 14.43437 | 14.09643 | 14.28396 |
| | | zz | -15.62955 | -16.30237 | -15.62649 | -16.00156 |
| | | xy | 7.67278 | 8.43102 | 8.97039 | 9.51356 |
| 34 | xx | xx | -13.79297 | -14.07462 | -14.52371 | -14.66452 |
| | | yy | 17.58200 | 17.39303 | 17.57695 | 17.44485 |
| | | zz | -3.78303 | -3.31841 | -3.05324 | -2.78033 |
| 35 | xx | xx | -7.14038 | -7.08547 | -6.96785 | -6.93653 |
| | | yy | 5.42599 | 5.48090 | 5.59853 | 5.62984 |
| | | zz | 1.71439 | 1.60457 | 1.36932 | 1.30669 |
| | | xy | -2.45215 | -2.91034 | -2.63795 | -2.91110 |
| 36 | xx | xx | 5.01563 | 4.82666 | 5.01058 | 4.87848 |
| | | yy | -1.23260 | -1.50825 | -1.95734 | -2.09815 |
| $q_x = q_y = 0, q_z \rightarrow 0$ | 12 | zz | 11.43288 | 11.61922 | 11.74777 | 11.84572 |

TABLE 4
Parameters for Crystals having Rutile Structure

| Parameter | Iron fluoride | Manganese fluoride | Magnesium fluoride | Rutile |
|-----------|---------------|--------------------|--------------------|--------|
| A_1 | 103.1 | 77.6 | 66.5 | 148.8 |
| B_1 | -3.1 | 2.3 | -6.0 | -15.5 |
| A_2 | 57.4 | 70.5 | 67.4 | 147.7 |
| B_2 | 14.0 | 2.0 | -3.8 | -36.6 |
| A_3 | 5.6 | 2.0 | 4.1 | 5.1 |
| B_3 | -6.0 | -5.4 | -0.4 | -2.7 |
| A_4 | 1.5 | 22.4 | 16.5 | 52.7 |
| B_4 | 1.2 | 4.0 | -1.4 | 22.9 |
| z_1 | 1.36 | 1.58 | 1.4 | 2.44 |
| z_2 | -0.68 | -0.79 | -0.7 | -1.22 |

TABLE 5
Vibration frequencies (in cm^{-1}) of crystals having rutile structure

| Assignment | Iron fluoride | | Manganese fluoride | | Magnesium fluoride | | Rutile | |
|-------------------|---------------|----------|--------------------|----------|--------------------|----------|------------|----------|
| | Calculated | Observed | Calculated | Observed | Calculated | Observed | Calculated | Observed |
| A_{1g} | 340 | 340 R | 341 | 341 R | 410 | 410 R | 612 | 612 R |
| B_{1g} | 73 | 73 R | 61 | 61 R | 92 | 92 R | 143 | 143 R |
| A_{2g} | 364 | — | 337 | — | 325 | — | 573 | — |
| B_{2g} | 496 | 496 R | 476 | 476 R | 515 | 515 R | 825 | 826 R |
| E_g | 257 | 257 R | 247 | 247 R | 295 | 295 R | 447 | 447 R |
| A_{2u} (T.O.) | 372 | 440 IR | 362 | 295 IR | 437 | 399 IR | 410 | 167 IR |
| E_{1u} (T.O.) | 192 | 200 IR | 159 | 159 IR | 247 | 247 IR | 168 | 183 IR |
| E_{2u} (T.O.) | 331 | 320 IR | 289 | 255 IR | 399 | 410 IR | 367 | 388 IR |
| E_{3u} (T.O.) | 480 | 480 IR | 362 | 363 IR | 460 | 450 IR | 509 | 500 IR |
| B_{1u}^1 | 330 | — | 288 | — | 453 | — | 430 | — |
| B_{1u}^2 | 55 | — | 99 | — | 189 | — | 206 | — |
| A_{2u} (L.O.) | 498 | — | 520 | 520 IR | 625 | 625 IR | 810 | 811 IR |
| E_{1u}^1 (L.O.) | 234 | — | 175 | 210 IR | 304 | 303 IR | 366 | 373 IR |
| E_{2u}^2 (L.O.) | 334 | — | 290 | 260 IR | 403 | 415 IR | 393 | 458 IR |
| E_{3u}^3 (L.O.) | 571 | — | 514 | 530 IR | 613 | 617 IR | 789 | 806 IR |

R = Raman effect, IR = Infrared spectra.

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