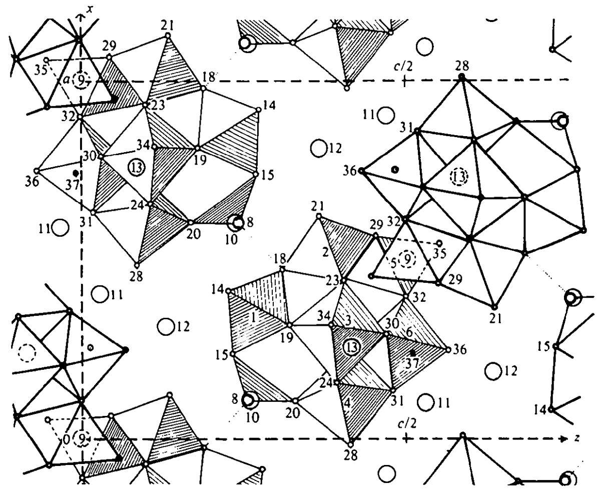

Fig. 3. Projection simplifiée de la structure dans le plan *ac* montrant les enchaînements d'anions. L'enchaînement associé au plan de symétrie $y_m = \frac{1}{4}$ est représenté en traits fins et les polyèdres sont ombrés. Le second, associé au plan $y_m = \frac{3}{4}$, est représenté en traits épais. Les numéros sont ceux des atomes d'oxygène (14 à 36), de Pb(8), des cations K^+ (9 à 13) et de $H_2O(37)$. La molécule $H_2O(38)$ se projette au même point que K(12). En tirets les limites de mailles. En pointillés la distance Pb—O(18) voisin.

– entre anions d'enchaînements de type différent: K(9), K(12).

– entre anions qui se correspondent dans la translation: K(13).

La Fig. 3 représente schématiquement cette disposition.

La position imprécise et très désordonnée des autres molécules d'eau (la majorité) dans les cavités de la structure est donc explicable.

De même, la densité étalée selon **b** (facteur anisotrope β_{22} élevé) de l'ion K(10) s'expliquerait par le fait qu'il soit lié d'un côté à deux anions d'un enchaînement au niveau de l'atome de plomb, de l'autre à des molécules d'eau voisines dans la cavité.

Références

Bally, R., Delettré, J. & Mornon, J. P. (1973). Programme *AFFINE*. Laboratoire de Minéralogie–Cristallographie. Univ. Paris VI.
Brown, G. M., Noë-Spirlet, M. R., Busing, W. R. & Levy, H. A. (1977). *Acta Cryst.* B33, 1038–1046.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
Donaldson, J. D., Donoghue, M. T. & Smith, C. H. (1976). *Acta Cryst.* B32, 2098–2101.
Donaldson, J. D., Moser, W. & Simpson, W. B. (1963). *Acta Cryst.* **16**, A22.
Gleizes, A. & Galy, J. (1979). *J. Solid State Chem.* **30**(1), 23–33.
International Tables for X-ray Crystallography (1974). Tome IV, pp. 148–151. Birmingham: Kynoch Press.
Jeannin, Y., Launay, J. P. & Seid Sedjadi, M. A. (1980). *Inorg. Chem.* **19**, 2933–2935.
Keggin, J. F. (1934). *Proc. R. Soc. London Ser. A*, **144**, 75–100.
Leciejewicz, J. (1961). *Acta Cryst.* **14**, 66.
Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain-la-Neuve, Belgique.
Rollins, O. W. (1966). Thesis. Georgetown Univ., Washington DC.
Schouten, A. (1980). Thèse d'Etat. USTL, Montpellier.
Tourné, C. M. & Tourné, G. (1968). *C. R. Acad. Sci. Sér. C*, **266**, 1363–1365.
Tourné, C. M. & Tourné, G. (1969). *Bull. Soc. Chim. Fr.* pp. 1124–1136.
Zonnevijlle, F. (1976). Thèse d'Etat. USTL, Montpellier.

Acta Cryst. (1982). **B38**, 1418–1422

A Theoretical Treatment of 'Orientational' Disorder for Routine Use

By Michael Jewess

British Telecom Intellectual Property Unit, 151 Gower St, London WC1E 6BA, England*

(*Received* 11 *September* 1981; *accepted* 11 *December* 1981)

Abstract

Many crystals are known in which diatomic or polyatomic ions are 'orientationally' disordered. General principles are presented which must govern the precise positions among which the ions are disordered, if short-range ordering is ignored. These principles are applied, by way of example, to four crystals, namely the room-temperature forms of ammonium chloride, tetramethylammonium trichloromanganate(II) (NMe_4MnCl_3), scawtite [$Ca_7(Si_6O_{18})(CO_3).2H_2O$], and bis-

---

* Address for correspondence purposes only, not an institution where the work was undertaken.

0567-7408/82/051418-05$01.00

(adiponitrile)copper(I) nitrate $\{Cu[NC(CH_2)_4CN]_2NO_3\}$. In these crystals, the disordered ions are, respectively, NH_4^+, NMe_4^+, CO_3^{2-} and NO_3^-. It is shown that the structure analyses reported for the latter three crystals were based on physically unfeasible assumptions about the positions among which the ions are disordered. It is suggested that this explains the problems encountered in each case, and that routine use of the general principles here presented should improve the reliability of future refinements of structures of this type.

1. Introduction

Many crystals are known in which diatomic or polyatomic ions are 'orientationally' disordered. Parsonage & Staveley (1978, pp. 269–456) have reviewed such crystals extensively.

A classic case of orientational disorder is NH_4Cl-II, the stable form of ammonium chloride at room temperature. On the basis of single-crystal neutron diffraction, Levy & Peterson (1952) concluded that the structure is of the CsCl type with space group *Pm*3*m*. Each NH_4^+ ion is surrounded by a cube of Cl^- ions at the centre of which the point-group symmetry is *m*3*m*. No distortion of the NH_4^+ ion can give it *m*3*m* symmetry, and its apparent symmetry is explained by disordering. The NH_4^+ ions take up with equal probability ($\frac{1}{2}$) the positions ('orientations') shown in Fig. 1, so that the average species 'seen' in the diffraction experiment has all the symmetry elements required. Physically, one considers the two positions to correspond to mutually equivalent potential minima of depth $\gg kT$ in which an ion may librate.

The twofold disordering is confirmed by the thermodynamic evidence [see Parsonage & Staveley (1978, pp. 311–315) and Callanan, Weir & Staveley (1980)]. Heat-capacity measurements indicate that the anomalous molar entropy change associated with the λ transition ($T_\lambda = 242{\cdot}5$ K) from the low-temperature III phase to the II phase is fairly close to $R \ln 2$, which is the configurational entropy change predicted for a transition of the NH_4^+ ions from ordering to twofold disordering. [It is generally the case that in order–disorder transitions the observed anomalous entropy change is dominated by the configurational term, the vibrational term being relatively minor. For a fuller discussion see Newns & Staveley (1966) and Parsonage & Staveley (1978, pp. 101–104).]

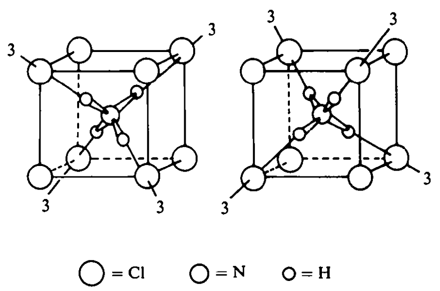

Fig. 1. The positions among which the NH_4^+ ions are disordered in NH_4Cl-II.

In analysing the diffraction results for other structures in which there is orientational disorder, crystallographers have usually assumed, at least in the first instance, that the disordering is closely analogous to that in NH_4Cl-II and other classic cases. It will be shown in this paper that NH_4Cl-II is a special case and that a close analogy with NH_4Cl-II is *not* to be expected in general. In particular, it will be shown that the disordering in three individual cases is necessarily qualitatively more complex. These cases are the room-temperature forms of tetramethylammonium trichloromanganate(II), scawtite and bis(adiponitrile)copper(I) nitrate, which contain, respectively, disordered Me_4N^+, CO_3^{2-} and NO_3^- ions.

2. General principles

Each of the positions among which an ion is disordered corresponds to a minimum in its potential energy. The potential-energy function is in detail extremely complex because of cooperative interactions between the ions leading to short-range ordering. The approach adopted here is to ignore such interactions. The potential energy can then be taken to derive from the interaction of the ion with an environment having point-group symmetry as determined by diffraction.

Within the limits of the approximation, stationary values of the potential energy (minima, maxima or saddle points) will usually, although not always, be related to coincidences between symmetry elements of the free-space ion with symmetry elements of the crystal. In this respect, only the coincidence of *like* symmetry elements is significant (*e.g.* of a 2 axis of the ion with a 2 axis in the crystal). Coincidence of *unlike* symmetry elements (*e.g.* of a 2 axis of the ion with a 3 axis in the crystal or of an *m* of the ion with the plane formed by two intersecting 2 axes in the crystal) is not in itself significant. Further, coincidence of symmetry origins, or of a symmetry origin with a point in a symmetry axis or plane, is not in itself significant.

3. Application of these general principles to NH_4Cl-II

The positions of the NH_4^+ ion shown in Fig. 1 are unique in that a 3 axis in the crystal coincides with each of the N—H bonds of the ion (*i.e.* the 3 axes of the free-space ion). Any small displacement of the ion, whether rotational about N or involving translation of N, destroys at least three of these coincidences. The positions are seen to be physically feasible potential-energy minima.

4. Tetramethylammonium trichloromanganate(II), NMe_4MnCl_3

This compound (commonly known also as TMMC, short for tetramethylammonium manganese chloride) is perhaps one of the most-studied compounds of the last decade or so, principally because it is a remarkably good approximation to a one-dimensional Heisenberg antiferromagnet. Here, however, it is the condition of the NMe_4^+ ions which is of concern.

Morosin & Graeber (1967), on the basis of single-crystal X-ray diffraction, concluded that at room temperature the space group was probably $P6_3/m$ (hexagonal), a space group which required the NMe_4^+ ions to be disordered. They considered as less likely but not impossible the space group $P6_3$, which would *not* require disordering of the ions; but that possibility can now reasonably be disregarded in view of the subsequent clear identification of an order–disorder transition (T_λ = 126 K) by low-temperature X-ray diffraction (Peercy, Morosin & Samara, 1973) and heat-capacity measurements (Dunn, Jewess, Staveley & Worswick, 1978).

The need for disordering with space group $P6_3/m$ arises because the NMe_4^+ ions are associated with sites of $\bar{6}$ ($3/m$) symmetry. Morosin & Graeber refined the structure by the least-squares method on the assumption that the ions were disordered among two equivalent positions for each of which (as illustrated in Fig. 2):

(*a*) an N—C bond (corresponding to a 3 axis of the free-space ion if internal rotation about the bond is ignored) coincides with the 3 axis of the site; and

(*b*) the N atom lies precisely in the site.

In other words, the only positional parameters of NMe_4^+ which were varied during refinement were the *z* coordinate of the C atom in the site 3 axis and the *x*, *y* and *z* coordinates of one of the other three C atoms.

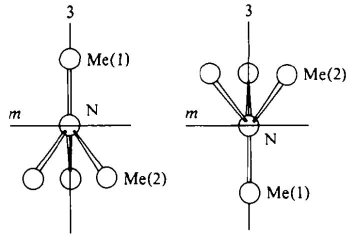

Fig. 2. The scheme for disordering the NMe_4^+ ions in NMe_4MnCl_3 proposed by Morosin & Graeber (1967). The ions are disordered with equal probability ($\frac{1}{2}$) among the positions shown. In each position, N—Me(1) coincides with the 3 axis of the site and also the mirror plane of the site passes through N.

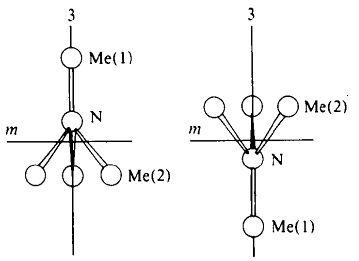

Fig. 3. Scheme proposed herein for twofold disordering of the NMe_4^+ ions in NMe_4MnCl_3. The ions are disordered with equal probability ($\frac{1}{2}$) among the positions shown. In each position, N—Me(1) coincides with the 3 axis of the site (as in Fig. 2) but N is displaced from the mirror plane of the site.

The use of constraint (*a*) is justifiable by reference to the general principles of § 2, since it relates to the coincidence of like symmetry elements. However, this is not the case for constraint (*b*); and therefore the positions for which both of conditions (*a*) and (*b*) are met cannot correspond to potential-energy minima, except accidentally and approximately. It follows that Morosin & Graeber's refinement procedure was improperly constrained.

In the nature of a least-squares refinement, the improper constraining of one or more parameters tends to lead to unusual values of those other parameters which *are* varied. It is therefore not surprising that Morosin & Graeber's final anisotropic thermal parameters for the C atoms were so large as require special comment. Morosin & Graeber believed that these implied some additional disordering beyond that shown in Fig. 2, of a type not clearly specified.

It is now suggested, as one possibility, that had the refinement been carried out subject only to constraint (*a*), then the thermal parameters might well have been normal. Such a refinement would have involved the varying of only one additional parameter. The result of such a refinement would have been a scheme of disordering of the type shown in Fig. 3.

Another possibility is that the NMe_4^+ ions are not *two*fold disordered at all, but *three*fold disordered, according to a scheme of the type shown in Fig. 4. In this, each position of the ion corresponds to the

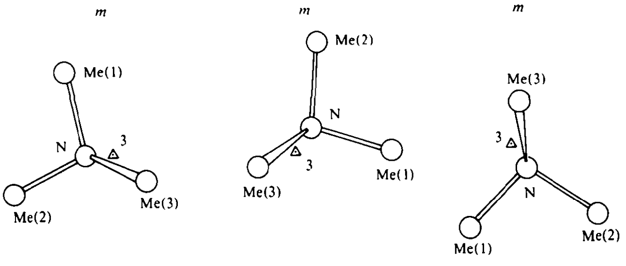

Fig. 4. Scheme proposed herein for threefold disordering of the NMe_4^+ ions in NMe_4MnCl_3. The ions are disordered among the positions shown with equal probability ($\frac{1}{3}$). In each position, N—Me(1) and N—Me(2) lie in the mirror plane of the site. N—Me(3) rises out of the plane, obscuring in the figure the fourth N—Me which is related to the third by the plane.

coincidence of a mirror plane of the free-space ion with the mirror plane of the site. The thermodynamic evidence, in fact, somewhat favours threefold disordering. The anomalous molar entropy change calculated by Dunn, Jewess, Staveley & Worswick for the order–disorder transition ($T_\lambda = 126$ K) is $R \ln 2{\cdot}8$. While this value is not so much above $R \ln 2$ that it is necessarily inconsistent with twofold disordering of the ions above the transition, it is of course much closer to $R \ln 3$, which is the molar configurational entropy change expected for a threefold disordering process.

The contrast between the present case and that of NH_4Cl-II is considerable. In the latter, it is feasible that there should be potential-energy minima for two positions of the ion for each of which the central atom lies in the symmetry origin of the site; it is a special case because of the close relationship of the ion and site symmetries (both cubic). In NMe_4MnCl_3, as in the two crystals discussed in §§ 5 and 6 below, such minima are not feasible, and to this extent the disorder can be said not to be purely 'orientational'.

5. Scawtite, $Ca_7(Si_6O_{18})(CO_3).2H_2O$

Pluth & Smith (1973) refined the room-temperature single-crystal results on this compound in the monoclinic space group *I*2/*m*. For this space group, the CO_3^{2-} ions must be associated with sites of 2/*m* symmetry, and must therefore be disordered. Pluth & Smith evidently performed their refinement on the assumption that the ion was disordered among two positions for each of which:

(*a*) of the three C—O bonds, one lies in the mirror plane of the site, while the other two are related by that plane (one of the three 'vertical' mirror planes of the free-space ion thereby coinciding with the mirror plane of the site); and

(*b*) the C atom lies precisely in the site.

On the basis of the general principles presented in § 2 it is now suggested that Pluth & Smith should have applied only constraint (*a*) during their refinement, so as to arrive directly at a structure of the type shown in Fig. 5.

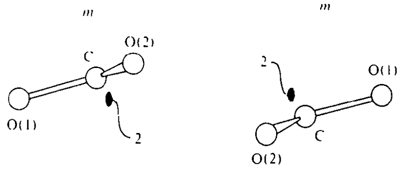

Fig. 5. Scheme proposed herein for disordering the CO_3^{2-} ions in scawtite. The ions are disordered with equal probability ($\frac{1}{2}$) among the positions shown. In each position, C—O(1) lies in the mirror plane of the site and C—O(2) rises out of the mirror plane, obscuring the third C—O which is related to the second by the plane. Due to the crystal field, the projection on the site mirror plane of angle O(1)—C—O(2) necessarily deviates *slightly* from 180°.

Pluth & Smith's refinement led to positional parameters which implied an unacceptably large distortion of the CO_3^{2-} ion from a planar equilateral triangle, and to thermal parameters for all the atoms of the ion which were larger than expected. They suggested an *ad hoc* explanation of these difficulties broadly along the lines of the present Fig. 5, while apparently regarding the need for this as tending to throw doubt on their refinement as a whole. They expressed their final conclusions cautiously, leaving open the question of whether the space group was *I*2/*m* at all, despite the fact that they had abandoned refinement in the alternative space group *Im* (with ordered CO_3^{2-} ions) because *R* had increased in the first least-squares cycle. The present discussion provides a theoretical explanation of the abnormal parameters and probably settles the space group as *I*2/*m*.

6. Bis(adiponitrile)copper(I) nitrate, $Cu[NC(CH_2)_4CN]_2NO_3$

Kinoshita, Matsubura, Higuchi & Saito (1959) investigated the room-temperature crystal structure of this compound by single-crystal X-ray diffraction. They deduced the orthorhombic space group *Pnnn*, which required the NO_3^- ions to be associated with sites of 222 symmetry and therefore to be disordered. They attempted to determine the precise positions among which the ions were disordered by trial structure factor calculations. They appear to have considered various twofold- and fourfold-disordered schemes, for each of which disordering was among positions wherein:

(*a*) one N—O bond (corresponding to a 2 axis of the free space ion) coincides with a 2 axis of the site;

(*b*) the ion lies in a plane perpendicular to another of the 2 axes of the site; and

(*c*) the N atom lies precisely in the site.

Best agreement between calculated and observed structure factors was obtained for a scheme of *fourfold* disordering.

However, the general principles of § 2 indicate that, of (*a*) to (*c*), only (*a*) is justifiable as a basis for devising trial schemes. It follows that one must regard fourfold disordering as unproven, and that it is possible that the

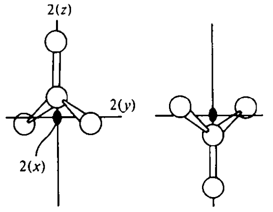

Fig. 6. Scheme proposed herein for disordering the NO_3^- ions in bis(adiponitrile)copper(I) nitrate. The ions are disordered among the positions shown with equal probability ($\frac{1}{2}$). In each position, one N—O coincides with 2(*z*).

ions are twofold disordered. Such twofold disordering would be among positions satisfying precisely only condition (*a*) above, according to a scheme of the type shown in Fig. 6, or of an analogous type in which in each position one N–O bond coincides with the site $2(x)$ or $2(y)$ axis.

The above critique of the conclusions of Kinoshita *et al.*, permits a simpler and more plausible interpretation than would otherwise be possible of the heat-capacity results obtained by Jewess, Lee-Bechtold & Staveley (1980). These workers observed a heat-capacity anomaly between 37 and 70 K for which the molar anomalous entropy gain was near to R ln 2. No other significant heat-capacity anomalies were observed elsewhere in the entire range 1·5–307 K. The likely significance of these results, then, is that:

(1) between 37 and 70 K, an ordered arrangement of NO_3^- ions passes over into one in which the ions are twofold disordered; and

(2) between 70 and 307 K either (i) this twofold disordering persists, though of course with increasing NO_3^- librational amplitudes, or (ii) the ions tend towards a hindered rotational motion (such a change need not necessarily be sufficiently cooperative to cause a readily observable heat-capacity anomaly).

7. Conclusion

It is suggested that the latter three crystals discussed above are candidates for new structure analyses consistent with the general principles of § 2, and that these principles should be routinely applied for other crystals containing 'orientationally' disordered ions. The extra effort would not be great, involving only the use of simple symmetry arguments to identify those cases where a somewhat larger number of positional parameters needs to be varied than might otherwise be thought necessary. Refinements in such cases should then be less likely to produce self-evidently unsatisfactory positional or vibrational parameters, or to lead to an incorrect determination of the number of positions among which the ions are disordered.

The author is indebted to Dr L. A. K. Staveley of the Inorganic Chemistry Laboratory, Oxford, in whose laboratory he performed his own experiments on two of the four compounds discussed above, and who commented on both drafts of this paper. He also thanks Dr A. K. Cheetham of the Chemical Crystallography Laboratory, Oxford, for commenting on the first draft.

References

Callanan, J. E., Weir, R. D. & Staveley, L. A. K. (1980). *Proc. R. Soc. London Ser. A*, **372**, 497–516.

Dunn, A. G., Jewess, M., Staveley, L. A. K. & Worswick, R. D. (1978). *Disorder in Crystals*, by N. G. Parsonage & L. A. K. Staveley, pp. 365–366. Oxford: Clarendon Press.

Jewess, M., Lee-Bechtold, S. & Staveley, L. A. K. (1980). *J. Chem. Soc. Faraday Trans.* 2, **76**, 803–811.

Kinoshita, Y., Matsubura, I., Higuchi, T. & Saito, Y. (1959). *Bull. Chem. Soc. Jpn*, **32**, 1221–1226.

Levy, H. A. & Peterson, S. W. (1952). *Phys. Rev.* **86**, 766–770.

Morosin, B. & Graeber, E. J. (1967). *Acta Cryst.* **23**, 766–770.

Newns, D. M. & Staveley, L. A. K. (1966). *Chem. Rev.* **66**, 267–278.

Parsonage, N. G. & Staveley, L. A. K. (1978). *Disorder in Crystals*. Oxford: Clarendon Press.

Peercy, P. S., Morosin, B. & Samara, G. A. (1973). *Phys. Rev. B*, **8**, 3378–3388.

Pluth, J. J. & Smith, J. V. (1973). *Acta Cryst.* B**29**, 73–80.

Acta Cryst. (1982). B**38**, 1422–1427

Electron-Density Distribution and Anharmonic Vibration in Crystals of Potassium Trifluorocuprate(II)

By Kiyoaki Tanaka and Fumiyuki Marumo

The Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, *Midori-ku, Yokohama* 227, *Japan*

(*Received* 1 *August* 1981; *accepted* 17 *December* 1981)

Abstract

The anharmonic vibration of Cu^{2+} ions in Jahn–Teller-distorted $KCuF_3$ crystals and its effect on electron-density distribution is described. In a previous study [Tanaka, Konishi & Marumo (1979). *Acta Cryst.* B**35**, 1303–1308], the electron-density distribution around the Cu^{2+} ions was analysed assuming mixed

0567-7408/82/051422-06$01.00