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The Crystal Structure of Sodium Nitrate in the High-Temperature Phase

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The crystal structure of sodium nitrate in the high-temperature phase has been redetermined on the basis of X-ray diffraction data obtained at 290°C.[1] The nitrate groups seem to be statistically distributed between two twofold disordered, nonequivalent sets of position in the trigonal unit cell. The contribution to the entropy predicted on the basis of the statistical model is in good agreement with the corresponding value deduced from calorimetric data.

According to early investigations the high-temperature phase of sodium nitrate, which is stable above 276°C, has a rotationally disordered structure.[2,3] Siegel [4] concluded from a study of diffuse X-ray scattering that the structure is of the disordered aragonite type, in which the nitrogen atoms occupy positions (0,0,z) etc., the oxygen atoms positions (x,2x,z) etc. and the sodium ions positions (0,0,$\frac{1}{2}$) etc. in space group $R\bar{3}m$ (hexagonal indexing), corresponding to the special positions: 6*c*3*m*, 18*hm* and 3*b*$\bar{3}m$ according to the notation of the *Intern. Tables*. More recently, however, Shinnaka [5] concluded, also on the basis of a study of diffuse X-ray scattering, that the structure is rather of the disordered calcite type, as had been suggested by others [6] as a possibility. In this model the nitrogen atoms are at the origin *etc.*, the sodium ions at (0,0,$\frac{1}{2}$) *etc.* and the oxygen atoms in the positions (x,x,0) *etc.* in space group $R\bar{3}m$, corresponding to the special positions 3*a*$\bar{3}m$, 3*b*$\bar{3}m$, and 18*f*2, respectively. Both authors agree with previous investigators [1,7] that the molecular rotation (reorientation) about the three-fold axes is hindered, which is further in agreement with results of infrared spectroscopic [8] and NMR spectroscopic investigations.[9] See also Ref. 10.

At room temperature sodium nitrate has a rigid calcite structure. The space group is $R\bar{3}c$. See for example Ref. 11 and references therein. As the temperature is raised, the phase changes into the high-temperature phase by a gradual transition ending at about 276°C.[12–15] The intensities of reflections for which $h+k+l=2n+1$, become weaker in the transition region and disappear at higher temperatures.[1] The space group changes from $R\bar{3}c$ to $R\bar{3}m$, which indicates that the nitrate group occupies statistically at least two

positions in the high-temperature phase. The O—Na contact distance increases only by about 0.05 Å from the room temperature value, assuming a calcite-type structure and an N—O bond length of 1.25 Å.[11] Thus it seems quite likely that the nitrate groups occupy, at least partly, positions of the disordered calcite-type in the high-temperature phase.

In the aragonite structure the nitrate groups are displaced along and rotated about the trigonal axes from the positions held in the calcite structure (in order to obtain an acceptable Na—O contact distance). The fact that the room temperature phase has a calcite type structure may suggest that the nitrogen atoms and the cations repel each other, as has been noted for potassium nitrate and nitrite (accompanying paper). Apparently an elongation of the c-axis may thus make aragonite positions accessible. Whereas the a-axis changes only little on heating, the c-axis exhibits a more pronounced increase, especially in the temperature region close to 276°C.[13] It seemed therefore possible that aragonite-type positions might also become accessible in the high temperature phase.

RESULTS AND DISCUSSION

A series of calculations based on least squares methods was performed, using the corrected X-ray diffraction data obtained by Tahvonen from a powder sample at 290°C.[1] The structure factors were computed according to the relationship $F_{cal}=X_1 \cdot F_A+X_2 \cdot F_C$, where X_1 is the "aragonite character", *i.e.* the fraction of the nitrate group occupying positions of the aragonite-type in the average, and $X_2=1-X_1$ is the "calcite character". F_A and F_C are the structure factors representing the two-fold disordered aragonite-type structure and the two-fold disordered calcite-type structure, respectively. In both structures the planes of the oxygen atoms of a nitrate group are perpendicular to the trigonal axis. In the calcite structure the nitrate group is planar, while in the aragonite structure this is not a requirement, although it was assumed to be planar. Values of the x and y parameters were calculated on the basis of an apparent N—O bond length of 1.22 Å, as was observed in the high-temperature phase of potassium nitrate. (Recently a value of 1.215 ($\sigma=0.006$) Å was reported for sodium nitrate at 200°C.[11]) The unit cell dimensions are: $a=5.087$ Å and $c=8.84$ Å, corresponding to three molecules per unit cell.[13] The form factors for the neutral atoms published by Hanson *et al.*[16] were used. These were multiplied by constant weight factors, corresponding to assigning excess charges of the following somewhat arbitrary values (in electron units) to the atoms: Na: 0.8, N: 0.4 and O: −0.4. Similar procedures were adopted in the cases of KNO_2 and KNO_3. Recently excess charges not much different from those quoted above were obtained for sodium nitrite from infrared dielectric dispersion measurements.[17]

As free parameters in the L.S. refinements were left the z coordinate of the nitrate group occupying aragonite-like positions, isotropic temperature factors of the atoms and the scale factor. Overlapping reflections had to be excluded in the refinement, although calculated amplitudes for these reflections were incorporated in a final series of L.S. refinements in an attempt at obtaining as good agreement as possible between all experimental and calculated data.

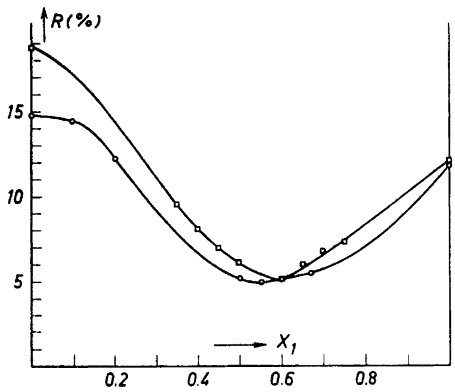

Fig. 1. *R*-factor *versus* X_1 (X_2). X_1=fraction of the nitrate group with oxygen atoms in positions of the type (x,2x,z). X_2=fraction of the nitrate group with oxygen atoms in positions of the type (x,x,0). Isotropic temperature factors. For the upper curve: B(Na)=B(N)=B(O). For the lower curve: B(N)=B(O).

The reflections were weighted according to standard procedures. As a result Fig. 1 was obtained, showing the *R*-factor plotted against X_1, which was kept as a fixed parameter in the L.S. refinements. Clearly, the agreement between observed and calculated quantities is much better for $X_1=0.5$ than for $X_1=0$ or $X_1=1$, as may be expected according to the previous discussion.

Values of positional and thermal parameters are listed in Table 1, and values of observed and calculated structure factors in Table 2. The temperature factor values of oxygen are considerably higher for $X_1=0$ or $X_1=1$ than for $X_1=0.55$. This would be expected if the importance of the oxygen positions was overestimated in the former cases.

Table 1. Positional and thermal parameters. Hexagonal axes. E.s.d. in parentheses. $X1=0.55$, apparent N−O bond length = 1.22 Å (ass.).

Atom	x	y	z	B (Å²)
Na	0	0	0.5	2.7 (0.66)
N1	0	0	−0.025	3.1
O1	0.1389 (calc.)	0.2778 (calc.)	−0.025 (0.006)	3.1 (1.2)
N2	0	0	0	3.1
O2	0.2405 (calc.)	0.2405 (calc.)	0	3.1

Finally a L.S. refinement was performed with the nitrate groups in calcite-type positions only, using *anisotropic* temperature factors for the oxygen atoms, while B(Na)=B(N). An *R*-value of 6.3 % was obtained, significantly higher than the minimum value of 5.0 % obtained for the previous model. For potassium nitrate in phase I an analogous result was obtained. The following discussion will thus primarily be based on the assumption that the nitrate group occupies statistically both types of position in the unit cell in the high temperature phase of sodium nitrate.

Fig. 2 shows the statistical distribution of the atomic equilibrium positions. The corresponding values of some of the interatomic distances are listed in

Table 2. Observed and calculated structure factors. Basic parameter values are those listed in Table 1. The calculated average values for overlapping reflections are based on the formula

$$\left(\frac{\sum p(HKL)\cdot F_c^2(HKL)}{(1/N)\cdot\sum p(HKL)}\right)^{\frac{1}{2}}$$

where $p(HKL)$ denotes the multiplicity of the corresponding reflection, and N is the number of overlapping reflections over which the summation is taken. $R=0.049$, $X1=0.55$.

H K L	$F_o(HKL)$	$F_c(HKL)$		*H K L*	$F_o(HKL)$	$F_c(HKL)$	
1 0 1	12.2	12.66		0 0 6	32.0	35.64	31.85
0 1 2	54.6	54.83		0 3 0		15.90	
0 0 3	37.0	37.79		2 0 5	8.4	8.38	
1 1 0	23.5	20.73		2 1 4	15.3	13.45	
0 2 1	28.2	28.01		0 3 3	11.4	12.12	13.60
1 0 4	43.5	40.38	44.27	3 0 3		6.17	
2 0 2		18.13		1 1 6	19.4	10.26	19.34
1 1 3	18.3	19.04		2 2 0		18.72	
0 1 5	18.7	3.20	18.28	1 0 7	12.7	1.65	15.12
2 1 1		15.67		1 2 5		13.47	
0 2 4	15.6	4.65	13.46	1 3 1		2.76	
1 2 2		11.18		3 1 2	17.5	16.12	
				2 2 3	1.9	3.29	

Table 3. Intermolecular distances in the high-temperature phase (290°C). $d(N-O)=1.25$ Å (ass.). Other basic parameter values are taken from Table 2. E.s.d. based on $\sigma(z_{01})$ in parentheses. Hexagonal axes.

	Distance (Å)
O1(x,2x,z)—Na(1/3,2/3,1/6)	2.39 (0.038)
O1(x,2x,z)—Na(2/3,1/3,—1/6)	2.84 (0.023)
O2(x,x,0)—Na(1/3,2/3,1/6)	2.45
O2(x,x,0)—Na(2/3,1/3,—1/6)	2.45
N1(0,0,z)—Na(2/3,1/3,—1/6)	3.19 (0.028)
N2(0,0,0)—Na(2/3,1/3,—1/6)	3.29
N1(0,0,z)—Na(0,0,—1/2)	4.20 (0.053)
N2(0,0,0)—Na(0,0,1/2)	4.42
O1(x,2x,z)—O1(1/3—x,2/3—2x,—1/3—z)	2.54 (0.07)
O1(x,2x,z)—O1(x,1—x,z)	2.93
O1(x,2x,z)—O2(0,1—x,0)	2.84 (0.04)
O2(x,x,0)—O1(1/3—x,2/3—2x,—1/3—z)	2.86 (0.05)
O2(x,x,0)—O2(1—x,1—x,0)	2.59
O2(x,x,0)—O2(1/3,2/3—x,—1/3)	3.05

Table 3. The shortness of the Na—O contact distances indicates a relatively strong attraction between the sodium ions and the oxygen atoms, as is to be expected. The difference between the values of the two nonequivalent Na—O contact distances is not significant. The Na—O contact distance is thus about 0.05 Å longer than the corresponding room temperature value. This indicates that the motion of the molecules is also restricted in the high-temperature phase. The nitrate groups must *a priori* be expected to occupy special positions (in the average) in the unit cell because of the symmetry of the

Table 4. Intermolecular distances listed in Table 3 at intermediate temperatures. Hexagonal unit axes according to space group $R\bar{3}m$. (True space group is $R\bar{3}c$, $c(R\bar{3}c)=2c(R\bar{3}m)$). Unit cell data from Ref. 13. Calculated values. $d(N-O)=1.25$ Å (ass.).

	Dist. (Å) $t=23°C$	Dist. (Å) $t=150°C$	Dist. (Å) $t=200°C$	Dist. (Å) $t=225°C$	Dist. (Å) $t=250°C$
O1(x,2x,z)—Na(1/3,2/3,1/6)	2.40 (ass.)	2.40 (ass.)	2.40 (ass.)	2.40 (ass.)	2.40 (ass.)
O2(x,x,0)—Na(1/3,2/3,1/6)	2.40	2.42	2.42	2.43	2.44
O1(x,2x,z)—O1(1/3−x,2/3−2x,−1/3−z)	2.22	2.32	2.36	2.39	2.44
O1(x,2x,z)—O1(x,1−x,z)	2.91	2.92	2.92	2.92	2.92
O1(x,2x,z)—O2(0,1−x,0)	2.83	2.83	2.84	2.84	2.84
O2(x,x,0)—O1(1/3,−x,2/3−2x,−1/3−z)	2.64	2.70	2.74	2.76	2.79
O2(x,x,0)—O2(1−x,1−x,0)	2.57	2.58	2.59	2.59	2.59
O2(x,x,0)—O2(1/3,2/3−x,−1/3)	2.91	2.95	2.97	2.98	3.01

attractive field produced by the sodium ions. It is, however, possible, that the interaction with the remaining part of the lattice will cause a small, time-dependent departure from these positions. Because of the thermodynamic equilibrium, which is expected to exist in the present case, all statistical positions of the nitrate groups indicated in Fig. 2 must be occupied in the time average. This is thought to occur through molecular reorientations about the three-fold axes coupled with a motion along the c-axis, as has been pointed out by Tahvonen,[1] because a simple rotation about the three-fold axes will produce too short Na—O distances. In the equilibrium positions the molecules execute anisotropic, librational (and translational) motion (see, *e.g.*, Ref. 11) with the result that they may pass over the potential hill into alternative positions as noted above. The mean reorientational frequency is generally observed to be low on a thermodynamic scale (*cf. e.g.*, results presented in Ref. 9). To ease the reorientational process the molecular motion is probably coupled to some extent. Thus the existence of the second order transformation leading to the present phase, indicates increasing cooperation of the molecules in the solid with temperature. From an energetic point of view, however, simultaneous reorientation of the molecules in an extended region of space is very unlikely. Instead, the reorientation process should be seen as fluctuations involving clusters of molecules.[18]

Because of the rather strong repulsive effect of the O—O interactions, molecular configurations involving relatively long O—O distances are expected to occur more frequently than others. As an average, however, the two statistical sets of position of the nitrate groups are approximately equally populated.

Two of the intermolecular O—O distances listed in Table 3 are considerably less than 2.8 Å, which is twice the van der Waals radius reported for oxygen.[19] The corresponding relative positions of the nitrate groups can hardly represent accessible states of the system at equilibrium. Thus in the following evaluation of the contribution to the entropy from the reorientational disorder of the nitrate groups (configurational entropy) these positions will be excluded. The number of accessible configurations, W, in a large system containing $N1$ molecules occupying one type of statistically equivalent positions and $N2$

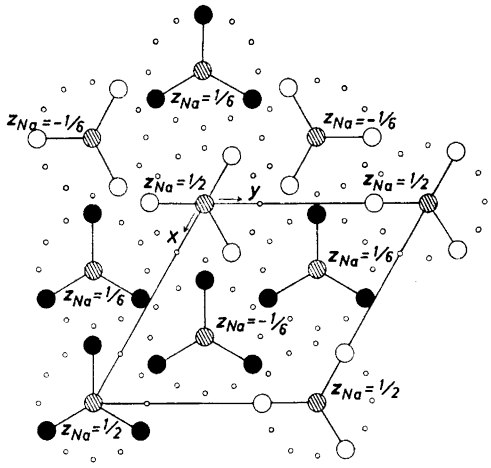

Fig. 2. Model of the statistical structure of sodium nitrate at 290°C. Small circles represent statistical equilibrium positions of the oxygen atoms. An acceptable configuration of nitrate groups is shown. For neighbouring atoms on a common threefold axis: $z_{Na}-z_N=\pm\frac{1}{2}$ (NO_3^- in calcite type positions: open circles for the oxygen atoms) and $z_{Na}-z_N\approx\pm\frac{1}{2}$ (NO_3^- in aragonite type positions: Filled circles for the oxygen atoms). Hexagonal axes.

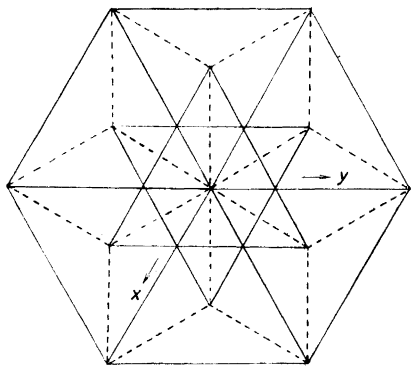

Fig. 3. Model used in the determination of the configurational entropy. The full lines represent forbidden, relative oxygen positions of the type $(x,x,0)$. The broken lines represent forbidden, relative oxygen positions of the type $(x,2x,z)$. Hexagonal axes. Equivalent microsystems are centred at (1/3,2/3,2/3) *etc.* and at (1,2,0) *etc.*

molecules occupying the alternative set, may then be represented by the following equation (more details will be given elsewhere)

$$W = g_1^{N_1}\, g_2^{N_2}\, \frac{N!}{N_1!N_2!}\,(1-S) \qquad (1)$$

where g_1 is the number of orientations each molecule in set 1 can take statistically, g_2 is the corresponding number for a molecule in set 2 and $N=N_1+N_2$. S is the number of forbidden configurations included in the total number of configurations implied statistically divided by this number, which is equal to the product of the first three factors on the right-hand side of eqn. (1). Thus S is equal to zero if there are no restrictions of the present kind. S may be shown to be related to experimental quantities through the following equation

$$S = \sum \sum_{i=0}^{2} s_1^{2-i}\cdot s_2^{i} - \sum \sum_{i=0}^{3} s_1^{3-i}\cdot s_2^{i} - \sum \sum_{i=0}^{4} s_1^{4-i}\cdot s_2^{i} \qquad (2)$$

plus terms up to N'th degree, where $s_1=X_1/g_1$, $s_2=X_2/g_2$, $X_1=N_1/N$ and $X_2=N_2/N$. The summations should be taken over all terms of second, third degree *etc.*, corresponding to the forbidden configurations. Terms of fourth

degree and higher are divided into groups of different origin and sign. In special cases terms of odd degree drop out, whilst each of the remaining types reduces to a single group.

The configurational entropy may then be obtained by the following formula:

$$\Delta S_c = k \ln W,$$

where k is the Boltzmann constant.

However, the evaluation of S according to (2) is rather complicated for a large system (except in a few trivial cases, where W is a small number). In numerical calculations simplifications will generally have to be made. Thus in order to estimate a value of $\Delta S_c(\ln W)$ the system may be broken into independent, equivalent "microsystems", whereby $1-S=(1-s)^n$, where n is the number of such microsystems; s represents the microsystem and is given by an equation similar to (2). Although correction terms may be included, the approximation given above is a poor one for W (or S), when n is a large number. Calculations based on some chosen examples, showed, however, that $(1-S)^{1/n}$ approached rather quickly a practically constant value for increasing values of N (and n). The nearly constant value was found to be little different from that of $1-s$, calculated on the basis of a microsystem of two lattice sites, provided $g=g_1+g_2$ was chosen larger than two. For the purpose of calculating values of the entropy, for which $(1-S)^{1/n}$ is the significant quantity because of the logarithmic form of eqn. (3), the indicated approximation is probably satisfactory to use in most cases, provided $g>2$, in view of the uncertainty in the corresponding measured data. The cases where $g=2$ are rather trivial in this respect and may, subject to restrictions of the present kind, give rise to only a few distinct configurations (see below).

Fig. 3 represents the basic system used in the evaluation of the configurational entropy of sodium nitrate at 290°C. The lines connecting two and two lattice sites represent forbidden oxygen-oxygen positions within the system. The central portion indicates the four positions occupied by a nitrate group in the time average. The system gives rise to terms in the $(1-s)$-equation up to 13'th degree. Since the "highdegree" terms have only a small influence on the value of s, terms of a degree higher than 7 were ignored. The more important terms shared among several subsystems were properly weighted. In the present case

$$g_1 = g_2 = 2,\ X_1 = 0.55,\ X_2 = 0.45,\ \text{and}\ n = N/6.$$

By using Stirlings formula *etc.*, we obtain finally

$$\Delta S_c = k \ln \left\{ {g_1}^{N_1} \cdot {g_2}^{N_2} \cdot \frac{N!}{N_1! N_2!} \cdot (1-s)^n \right\}$$

$$= R\,(X_1 \ln g_1/X_1 + X_2 \ln g_2/X_2) + (R/6) \cdot \ln (1-s)$$

$$= (2.745-0.850)\ \text{cal/mole deg.} = 1.90\ \text{cal/mole deg.}$$

For an error of 5 % in X_1 and 30 % in $(1-s)$ (arbitrarily chosen) the maximal error in ΔS_c becomes

$$\Delta^2 S_c(\max) = (0.02 + 0.13) \text{ cal/mole deg.} = 0.15 \text{ cal/mole deg.}$$

It may be mentioned in this connection that molecules in interfacial positions or bounded by lattice imperfections *etc.* may have considerably more orientational freedom than what has been assumed here. This should give rise to a positive, temperature-dependent contribution to the configurational entropy. Since molecules in such positions generally represent a minor part of the total, the magnitude of this contribution is probably relatively small.

Ravich *et al.*[20] have obtained a value of 1150 cal/mole for the heat of transition of the second order phase transformation in sodium nitrate on the basis of differential thermal measurements. Graphical integration of the (anomalous) C_p *vs.* T curve obtained by Sokolov and Shmidt [14] gave the heat of change as 1185 cal/mole,[20] whereas Mustajoki [12] obtained a value of 944 cal/mole. By a similar integration values of the entropy of transition were obtained as 2.3 cal/mole deg. and 1.7 cal/mole deg., respectively. A value close to the former is to be expected from the C_p data of Reinsborough *et al.*,[15] which are in close agreement with those of Sokolov *et al.* The figures are not much different from those obtained from the corresponding values of the heat of transition divided by T_c=548°K. As an average value for the entropy of transition we obtain 2.1 cal/mole deg. These results depend on the chosen position of the base line connecting the C_p curve on either side of the transition. It is a common procedure to treat terms contributing to the heat capacity as being independent of each other. The thermal parts give rise to a monotonically increasing heat capacity with temperature. It is assumed that this is approximately true in the transition region and that this behaviour of the C_p curve may be approximately represented by the base line referred to above. (It may be, however, that the shape of the curve should be rather more like that of the curve representing the thermal expansion.[13] As a result a slightly smaller value than that given above should be obtained for the entropy of transition). The "anomalous" part of the heat capacity will then have to be attributed to some molecular disordering process, which is commonly believed to occur in the solid, as pointed out previously.

On this basis it is seen that the value of the entropy change predicted by the structural model deduced on the basis of the X-ray diffraction data etc. is in good agreement with the experimental value. A similar interpretation of the transition entropy is not possible on the basis of a disordered calcite type structure [5] or a disordered aragonite structure [4] alone, since only a few distinct molecular configurations are implied in either case.

It may be mentioned that order-disorder transitions also occur in solid potassium nitrate [21] and potassium nitrite.[22] In these cases the difference between the experimental value of the entropy change and the calculated is appreciably larger than what is found here. Since, however, the transitions in the former cases are isothermal, a larger discrepancy is to be expected compared with the present value.

A natural extension of the present work would be to study the crystal structure at intermediate temperatures by X-ray diffraction techniques. Table 4 lists some calculated values of intermolecular distances referred to

various temperatures. The values are based on a chosen N—O bond distance of 1.25 Å along with unit cell dimensions calculated from the data of Kantola and Vilhonen.[13] The z-parameter of the nitrate group was estimated for simplicity on the basis of an Na—O distance of 2.40 Å, the value obtained at room temperature. It appears that nitrate orientations originating in disordered oxygen positions of both types may be accessible according to the criterion used previously. Also, for the reason pointed out above, it seems necessary to introduce both types of disordered nitrate positions to explain the extra increase in the heat capacity, starting at temperatures below 200°C.

The full matrix least squares computer program used is that written by Gantzel, Sparks and Trueblood (*IUCr World List* No. 384) and adapted for UNIVAC 1107 by Chr. Rømming, Chemistry Department, University of Oslo. The Fourier programme was written by Gantzel and Hope (Department of Chemistry, University of California, Los Angeles, Calif., U.S.A.).

REFERENCES

1. Tahvonen, P. E. *Ann. Acad. Sci. Fennicae, A, I. Math-Phys.* **1947** No. 43.
2. Kracek, F. C., Posnjak, E. and Hendricks, S. B. *J. Am. Chem. Soc.* **53** (1931) 3339.
3. Bijvoet, J. M. and Ketelaar, J. A. A. *J. Am. Chem. Soc.* **54** (1932) 625.
4. Siegel, L. A. *J. Chem. Phys.* **17** (1949) 1146.
5. Shinnaka, Y. *J. Phys. Soc. Japan* **19** (1964) 1281.
6. Ketelaar, J. A. A. and Strijk, B. *Rec. Trav. Chim.* **64** (1945) 174.
7. Miekk-oja, H. *Ann. Acad. Sci. Fennicae, A, I. Math.Phys.* **1941** No. 7.
8. Hexter, R. M. *Spectrochim. Acta* **10** (1958) 291.
9. Andrew, E. R., Eades, R. G., Hennel, J. W. and Hughes, D. G. *Proc. Phys. Soc.* **79** (1962) 954.
10. Newns, D. M. and Stavely, L. A. K. *Chem. Rev.* **66** (1966) 267.
11. Cherin, P., Hamilton, W. C. and Post, B. *Acta Cryst.* **23** (1967) 455.
12. Mustajoki, A. *Ann. Acad. Sci. Fennicae, A, VI. Physica* **1957** No. 5.
13. Kantola, M. and Vilhonen, E. *Ibid. A, VI. Physica* **1960** No. 54.
14. Sokolov, V. A. and Shmidt, N. E. *Izv. Akad. Nauk. SSSR, Sektora Fiz.-Khim. Anal.* **26** (1955) 123.
15. Reinsborough, V. C. and Wetmore, F. E. V. *Australian J. Chem.* **20** (1967) 1.
16. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
17. Axe, J. D. *Phys. Rev.* **167** (1968) 573.
18. Cox, E. G., Cruickshank, D. W. J. and Smith, J. A. S. *Proc. Roy. Soc.* **A 247** (1958) 1.
19. Pauling, L. *Nature of the Chemical Bond.* Cornell University Press (1960).
20. Ravich, G. B. and Egorov, B. N. *Russ. J. Inorg. Chem.* **5** (1960) 1257.
21. Tahvonen, P. E. *Ann. Acad. Sci. Fennicae, A, I. Math.Phys.* **1947** No. 44.
22. Ray, J. D. and Ogg, R. A. *J. Phys. Chem.* **60** (1956) 1599.

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