

A, ions with complete octets; B, ions formed from covalences; (3) dissociation and reactions of electrically neutral atoms and molecules.

The following principles, which the space allowed does not permit me to discuss, give a satisfactory explanation of the inorganic complexes: 4. Atoms may form covalence groups with a larger number of covalences than the number of valence electrons of the central atom. 5. A valence electron may be transferred, either to form a negative ion which enters the complex or one that is exterior to the complex. 6. If the "donor" (Sidgwick) is an electrically neutral molecule (ammonia or water), it becomes a positive ion in the complex; if it is a negative ion (Cl^- , NO_2^-), it becomes electrically neutral in the complex. 7. The "acceptor," in every case, develops a negative charge for each covalence, which may be balanced by the positive charge of the "kernel" (Lewis), by the positive ions of the complex or by positive ions exterior to the complex.

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The Linear Thermal Expansion of a Single Crystal of Sodium Nitrate

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The results of a recent series of studies of the physical properties of sodium nitrate conducted by Kracek¹ and his colleagues² have firmly established the existence of a gradual transition in the crystalline salt between 150 and 280°. The transition appears to be practically completed at 275° but abnormal changes in the heat capacity and volume are distributed over an extended temperature interval below this critical point.

The basis for a satisfactory explanation of the phenomenon seems to have been found in the theoretical treatment by Pauling³ of the problem of the diatomic homopolar molecule free to rotate in an axially symmetrical field of force. His analysis together with the available x-ray evidence² makes it seem almost certain that during the transition interval the rotational degree of freedom of the nitrate ion about an axis normal to the plane of the group becomes excited. At the critical temperature this degree of freedom is fully excited and the nitrate ion begins to rotate about the trigonal axis of the crystal unit. The transition corresponds, therefore, to a change from oscillational to rotational motion for the nitrate ion.

One of the properties studied in detail by Kracek was the volume ex-

(1) Kracek, *THIS JOURNAL*, **53**, 2809 (1931).

(2) Kracek, Posnjak and Hendricks, *ibid.*, **53**, 3339 (1931).

(3) Pauling, *Phys. Rev.*, **36**, 430 (1930).

pansion of the salt. While his results serve admirably to demonstrate the existence of the transition they do not elucidate the very interesting question of the anisotropic expansion in various directions in the crystal. Such information is of considerable value in analyzing the nature of the changes which take place during the transition, and since a knowledge of the mechanism of these changes is of great importance in the theory of the solid state, we have undertaken a series of measurements of the expansion in several directions of known orientation in the crystal.

Material.—The sodium nitrate used in the experiments was recrystallized three times starting with the best material commercially available. It crystallizes easily so that single crystals of considerable size can be readily secured. A number of crystals were prepared and the clearest and most perfect ones were selected for use.

Apparatus.—The Pulfrich-Fizeau interference method as modified by the U. S. Bureau of Standards was employed in making the measurements. The principles of,

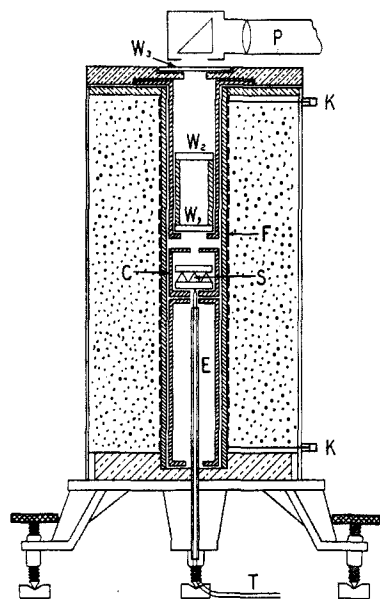


Fig. 1.—Apparatus for measuring linear thermal expansion.

and apparatus for, this method are described in the publications of the Bureau.⁴ The only departure from the equipment therein specified was in the design of the furnace which is shown in Fig. 1. A porcelain tube, F, wound with a helical nichrome coil, K, is mounted vertically in a sheet iron jacket and is surrounded with Sil-O-Cel. A smaller tube, E, supports the porcelain cup, C, which contains the interferometer plates, S. A small bore porcelain tube holding the platinum-platinrhodium thermocouple passes through the bottom of the cup, C, the junction being so adjusted that it nearly touches the lower interferometer plate. The upper end of the furnace is closed by another porcelain tube containing the fused silica windows W_1 and W_2 ; W_3 is a glass window.

The viewing apparatus is shown at P. The helium line at 5875.6 \AA . was used as a monochromatic source of illumination. With this light a change in length of $\approx 3 \times 10^{-6} \text{ cm}$. could be easily detected.

The thermocouple was checked in position in the furnace on the melting points of tin, aluminum and silver, and on the α - β inversion of quartz; it was also checked against a carefully calibrated refraction thermometer of fused silica. Temperatures were read on a Leeds and Northrup wall-type potentiometer which had been checked at the Bureau of Standards and are probably good to $\approx 1^\circ$ or better.

With this apparatus it is necessary to have three small specimens very nearly the same height. Preliminary experiments showed that the results obtained with a set of three small pyramids cut from one large crystal were more satisfactory than those obtained with specimens cut from three small crystals; hence for the final measurements a small slab was cut from a large crystal so that the normal to the surface of the slab co-

(4) Peters and Cragoe, *Bur. Standards Sci. Papers* (No. 393), **16**, 449 (1920); Peters and Boyd, *ibid.*, (No. 436), **17**, 677 (1922); Merritt, *ibid.*, (No. 485) **19**, 357 (1924).

incided with the direction in the crystal along which the expansion was to be determined. Three small pyramids were then cut from this slab. Although this method of preparation does not orient the specimens with great accuracy it proved to be quite satisfactory for the present purpose.

Results

The expansion was measured in three different directions: parallel to the a axis, parallel to the c axis and perpendicular to the rhombohedral faces ($10\bar{1}1$) and ($\bar{1}01\bar{1}$). For the first two directions two sets of specimens were examined; for the last direction but one was used.

The results obtained are given in Table I in the form of the increase in length per unit length and the true linear expansion coefficient; these values were taken from a smoothed curve drawn through the experimental points for all the determinations in a given direction. This procedure was rendered advisable by the fact that the curves for any single determination showed curious undulations, apparently connected with the efflorescence of the salt on heating, which were not reproducible and could be largely balanced out by combining the data for two runs. The curves themselves and the experimental points are shown in Fig. 2.

TABLE I
LINEAR EXPANSION OF SINGLE-CRYSTAL SODIUM NITRATE

t , °C.	Increase in length per unit length ($\Delta l/l_0$) in mm./m.		c axis	True linear expansion coeff. $\alpha \cdot 10^6$ at t°		
	(a axis)	($\perp 10\bar{1}1$ face)		(a axis)	($\perp 10\bar{1}1$ face)	(c axis)
18	0.0	0.0	0.0
50	.35	2.5	2.8	11.0	74	120
75	.62	4.4	5.7	11.6	76	122
100	.93	6.3	8.9	12.0	78	132
125	1.22	8.3	12.3	11.4	80	138
150	1.50	10.3	15.8	11.0	82	142
175	1.77	12.4	19.4	10.6	84	152
200	2.03	14.5	23.4	10.5	106	184
225	2.30	17.7	28.6	10.4	148	234
250	2.55	22.4	35.1	10.0	210	368
260	2.65	24.7	38.6	10.0	235	445
270	2.75	27.3	44.0	10.0	320	600
295	2.80	29.0	47.0	10.0	540	660

The variation of the expansion coefficients with temperature is shown in Fig. 3a.

Aside from the slight irregularities mentioned the results were, with one exception, strictly reproducible, not only on heating and cooling but also from sample to sample. Such variations as do appear are well within the possible error arising from the uncertainty of the orientation and the measurement of the expansion.

The one exception is the contraction of the crystal above the critical temperature in the direction of the a axis, which was not reproducible even for the same sample on heating and cooling.

Unfortunately the set of specimens for the direction perpendicular to the $10\bar{1}1$ face suffered some irregular behavior in passing through the critical point at 275° and the fringes were lost, hence no measurements above this temperature are available for this direction.

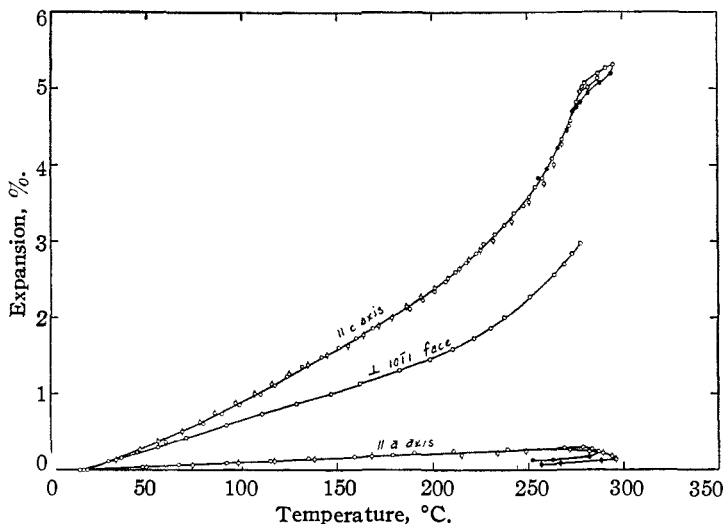


Fig. 2.—Linear expansion of single-crystal sodium nitrate in various directions in the crystal. O, first set of specimens; ◊, second set of specimens; ●, points obtained on cooling.

Discussion

The most striking feature of the data presented is the very large difference in expansion in the directions of the crystallographic axes. In the direction of the a axis the total expansion at 275° is only 0.3%, while perpendicular to this direction (parallel to c axis) it is 5% or 17 times as great. Anisotropy of this magnitude is extremely unusual, at least among the substances thus far described in the literature, and is to be accounted for by the abnormal increase in length along the c axis during the transition. It will be interesting to see whether, when other substances having the same type of transition are discovered, they will possess a similar behavior.

It is important to note that the effect of the transition along the a axis is extremely slight, if indeed it exists at all, since the expansion coefficient actually decreases slightly in the transition range. This fact together with the abnormal increase in length along the c axis leads to some important conclusions regarding the mechanism of the change.

In order to picture the relative motions of the various parts of the lattice it is necessary to have the structure of the lattice clearly defined. It appears to be well established that a number of nitrates, including sodium nitrate, owe their strong double refraction to the arrangement of the

nitrate groups in parallel planes. It also appears that the metal ions lie in planes parallel to, and alternating with, the planes of the NO_3 group.

If the interpretation of the x-ray data by Kracek, Posnjak and Hendricks is correct the abnormal expansion between 150 and 280° is indicative of an increasing amplitude of oscillation of the NO_3 ions in the plane of the group and perpendicular to this plane, that is, the oscillation is about the trigonal axis of the crystal unit. It is also probable that actual rotation is present for a small number of ions during the transition interval, the proportion of such ions increasing with temperature.

Applying these concepts to the expansion data one is led to conclude that the increasing amplitude of oscillation results in a marked separation of the planes of the nitrate ions and metal ions without any abnormal increase in the dimensions in the plane of the group. In other words the intermolecular forces which are affected are those acting between the alternate layers of nitrate and metal ions whereas the forces acting in those planes remain substantially unchanged.

A more exact description can be made along the lines of Pauling's theoretical treatment. As the temperature is increased the energy level, n , of the nitrate ion will also change. When $n + 1$ becomes greater than a certain critical value, which depends upon the moment of inertia and the constant of the potential function (V_0), the motion becomes rotational. As n approaches the transition value the eigenfunctions change completely in nature, becoming more nearly constant. This change increases the repulsive forces between alternate layers of nitrate ions and possibly between the layers of nitrate and metal ions resulting in a tendency to spread the crystal lattice as soon as an appreciable number of molecules have begun to rotate. But spreading the lattice decreases the forces between the layers and decreases V_0 . This permits more molecules to rotate and the effect builds up to give increasingly greater expansion

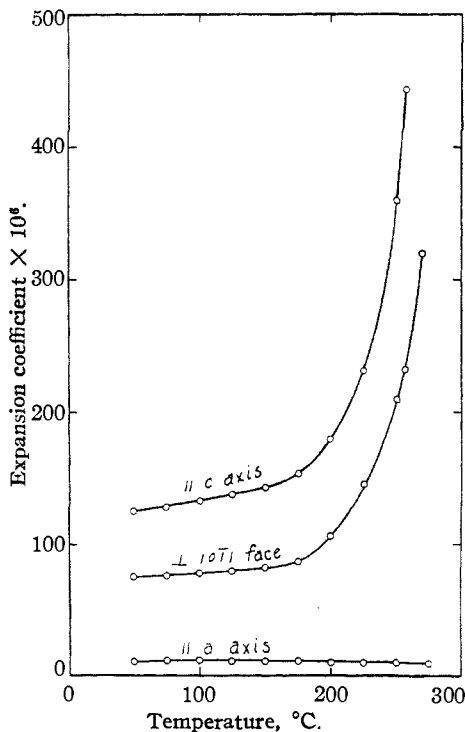


Fig. 3a.—True linear expansion coefficient of sodium nitrate in various directions in the crystals.

perpendicular to the planes of the NO_3 ions. When all the nitrate groups are rotating the effect is no longer observed.

So far rotation about an axis normal to the plane of the NO_3 group has been considered. The ion has two other rotational degrees of freedom about axes in the plane of the group but these are apparently degenerate, as pointed out by Kracek, Posnjak and Hendricks, and hence will not be considered.

Attention should also be called to the irreversible contraction observed in the direction of the a axis when the critical point is passed. This effect

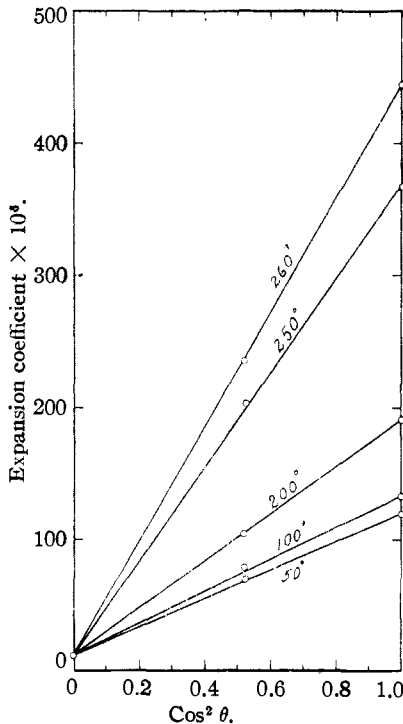


Fig. 3b.—True expansion coefficient α plotted as a function of $\cos^2 \theta$.

may be due to an actual contraction of the specimen but it is also possible that in this region the crystal becomes so soft that it can no longer support the weight of the upper plate of the interferometer. While no definite choice can be made at present between these explanations, the fact that the contraction was not reproducible with different specimens renders the latter hypothesis slightly more acceptable.

The abnormal increase in length along the c axis also leads to an appreciable decrease in α , that is, the angle between the axes of the true structural unit⁵ as Kracek, Posnjak and Hendricks have already noted. Specifically they found that α decreased from $47^\circ 14'$ at 25° to $45^\circ 35'$ at 280° . If we assume for 25° the axial ratio $a:c = 1:0.8297$ which corresponds to $\alpha = 47^\circ 14'$, values of the axial ratio and of α for 280° can also be obtained from the expansion data.

The axial ratio so computed is 0.8662, corresponding to an angle of $45^\circ 34'$, which is only one minute smaller than the angle calculated from the x-ray data. This agreement is most satisfactory.

As mentioned above the data for successive runs on the same set of samples and measurements on different sets gave results which showed that the effects observed were unquestionably reproducible. It can further be shown that the data for the three directions measured are consistent within themselves. The simplest manner of comparing the data for this purpose

(5) Cf. Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

is by means of the cosine-square law which states that in a crystal having hexagonal symmetry the expansion coefficient is a linear function of the square of the cosine of the angle between the direction of measurement and the principal axis of the crystal.

The expansion coefficients at a number of temperatures for the three directions studied are plotted against $\cos^2 \theta$ in Fig. 3b. In plotting these curves no correction has been made for the change in the angle θ with temperature but for the set of measurements in the direction perpendicular to the rhombohedral faces it has been assumed to be $43^\circ 46'$, the value at 25° , throughout. The neglect of this change is justified by the fact that it is quite small and introduces an uncertainty less than that in the orientations of the specimens along the a and c axes. It is obvious, however, from the figure that the results are consistent among themselves within the limit of experimental error.

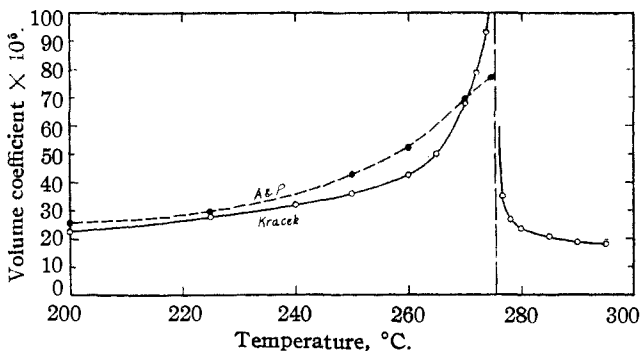


Fig. 4.—Volume expansion coefficient of sodium nitrate: O, Kracek direct determination; ●, Austin and Pierce, calculated from linear expansion coefficients along the crystallographic axes.

It is also possible to calculate the volume expansion of the crystal from the expansions along the directions of the crystallographic axes. Thus the coefficient of cubical expansion β is equal to $\alpha_3 + 2\alpha_1$ where α_3 and α_1 are the linear coefficients in the c direction and a directions, respectively. The values of β so calculated are shown by the dotted line in Fig. 4 where they are compared with the direct determinations of Kracek (solid line). The agreement is satisfactory considering the uncertainties inherent in each curve.

It may be worth mentioning in conclusion that our measurements of the temperature at which the transition is completed appeared to be nearer 278° than 275.5° as reported by Kracek. The difference is not serious and may arise from the fact that our temperature measurements were not so precise as his or may possibly be due to different definitions of the completion of the change.

Summary

It has been shown by means of linear expansion measurements in different directions in single crystals of sodium nitrate that the gradual transition occurring between 150 and 278° is most marked in the direction of the *c* axis and was not detected along the *a* axis. This is interpreted as indicating a separation of the layers of nitrate ions resulting from the change in the eigenfunctions caused by the rotation of the ion. The angle α is calculated to be 45°34' at 280° as compared with $\alpha = 45°35'$ obtained from the x-ray data by Kracek, Posnjak and Hendricks.

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Anomalous Electrolytes. I. The Electrical Conductivity of Solutions of Iodine and Cyanogen Iodide in Pyridine¹

BY L. F. AUDRIETH² AND E. J. BIRR

It has often been shown that substances which are usually designated as non-electrolytes, with reference to water as solvent, may in suitable media exhibit salt-like properties and yield conducting solutions. This anomalous behavior has been ascribed either to (1) a transformation of a *pseudo*-salt into a true salt, or (2) to reaction of the solute with the solvent with the resultant formation of solvated compounds of greater or lesser stability which conduct the electric current. Thus nitro compounds have been found to yield conducting solutions in ammonia³ and in hydrazine,⁴ whereas iodine and the cyanogen halides have been found to act as electrolytes in such solvents as liquid sulfur dioxide, arsenious chloride and sulfuryl chloride.⁵

In the first paper of this series the results of a preliminary investigation concerning the nature of solutions of iodine and cyanogen iodide in pyridine, as revealed by a study of their electrical conductivity, are presented.

Experimental

Materials.—The solvent, Pyridin purissimum Kahlbaum, was dried over solid potassium hydroxide and then distilled repeatedly from a solution of cadmium per-

(1) It is with pleasure that the authors acknowledge their indebtedness to Professor Paul Walden for his interest and encouragement and for his kindness in placing at their disposal the facilities of the laboratory.

(2) University of Illinois, Urbana, Illinois. National Research Council Fellow at the University of Rostock, 1931-1932. The aid of a fellowship grant from the National Research Council, Washington, D. C., is gratefully acknowledged.

(3) Franklin and Kraus, *Am. Chem. J.*, **23**, 279 (1900); **27**, 191 (1905); Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

(4) Hilgert, Thesis, Rostock, 1932.

(5) Walden, *Z. physik. Chem.*, **43**, 385, 409, 423, 445 (1903).