densation of the $In^+$ ions in this special way may just result in a minimum free energy of the compound.

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# Configuration of the Cyanide Ion in Potassium Zinc Cyanide
## A Neutron Diffraction Study

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A single-crystal neutron-diffraction study of the structure of cubic ($a = 12{\cdot}53$ Å) potassium zinc cyanide, $K_2Zn(CN)_4$, has been made with a view to studying the coordination of the cyanide ion in a complex metal cyanide. Four possible structural models have been tested on the basis of 96 *hhl* intensities. Model I, involving a freely-rotating cyanide ion, was ruled out quite easily. The other three models were refined by the method of least squares with individual isotropic temperature factors, and model II, with the cyanide-ion coordination of the type Zn–C–N–K–N–C–Zn, was found to give the best agreement between the observed and calculated structure factors. Model III, with the inverse coordination involving interchange of the C and N atoms, as well as model IV, with disordered cyanide ions, could be rejected. The structure has been further refined on the basis of model II with anisotropic thermal parameters. Zinc is tetrahedrally coordinated to four cyanide ions and the Zn–C–N group is linear. The C–N distance corrected for thermal motion is $1{\cdot}157 \pm 0{\cdot}009$ Å. Six nitrogen atoms form a trigonal antiprism around potassium.

### Introduction

The coordination of the cyanide ion in metal cyanides is a problem that has attracted the attention of investigators from various fields including X-ray diffraction, spectroscopy, and, more recently, neutron diffraction. In the case of alkali cyanides such as KCN (Sequeira, 1965), NaCN and RbCN (Bijvoet & Lély, 1940), and CsCN( Lély, 1942) which are cubic in their room-temperature phases, the question of specific coordination with the alkali metal ion does not arise, the neighbouring sites to the metal ion being statistically shared by C and N. In other cyanides, particularly the complex cyanides, it is often assumed that the polyvalent metal-ion coordination is with the carbon atom; this assumption is found in many textbooks of chemistry (Pauling, 1960). It may be mentioned here that on the basis of his infrared studies, Jones (1957*a*) has attempted to determine the cyanide-ion coordination in a series of cyanides, and although his studies favour the polyvalent metal-ion coordination with the carbon atom his rejection of the alternative coordination seems somewhat tentative.

It should be of interest to obtain conclusive evidence from diffraction studies regarding this point. In view of the fact that carbon and nitrogen have nearly the same X-ray scattering amplitudes, recent attempts to distinguish between carbon and nitrogen in X-ray structure determinations have been based on indirect criteria such as the reasonableness of the temperature factors (Rossmann, Jacobson, Hirshfeld & Lipscomb, 1959; Emerson & Britton, 1963) or the reasonableness of the bond-angles (Cromer, 1957) or bond lengths (Cromer & Larson, 1962), and have not been absolutely convincing. In a recent X-ray investigation of $CuCN \cdot NH_3$, Cromer, Larson & Roof (1965) have refined the structure for two alternative orientations of the cyanide group (involving interchange of the C and N atoms) and have chosen one of them on the basis of a marginally better *R* index and more sensible thermal parameters; they state, however, that 'the evidence is not overwhelming'.

Although neutron diffraction is better suited for this particular type of problem, distinguishing between carbon and nitrogen by neutron diffraction has been attempted only in the case of $K_3Co(CN)_6$ (Curry & Runciman, 1959). Although the conclusions of Curry & Runciman seem to be satisfactory, one would wish that the refinement of the alternative structure had been continued to the convergence of the parameters, before the criterion of the reasonableness of the temperature factors had been applied. In this investigation of the structure of $K_2Zn(CN)_4$ by neutron diffraction we have attempted to study the coordination of the cyanide ion in a complex metal cyanide to an accuracy higher than that attempted in any of the earlier investigations. Also, it was of interest to test the power of the neutron diffraction technique in distinguishing between various closely related structural models, for which this investigation offered an excellent opportunity.

The structure of $K_2Zn(CN)_4$ was studied by X-rays by Dickinson (1922) who assigned it to the space group *Fd*3*m*. No attempt was made to distinguish between carbon and nitrogen, nor was a dynamic model, with the cyanide ion freely rotating, tried. We have attempted to choose between the following four models:

I. Dynamic model with the cyanide ion freely rotating.
II. Static ordered model with the cyanide ion having a coordination of the type -Zn–C–N–K–N–C–Zn–.
III. Static ordered model with the cyanide ion having an inverse coordination -Zn–N–C–K–C–N–Zn–.
IV. Static disordered model which is an average of models II and III (This model is really not expected since the two ends of the cyanide ion are in widely different crystalline fields and the two cyanide-ion orientations are highly unlikely to correspond to identical energy states of the crystal).

## Experimental

Potassium zinc cyanide, $K_2Zn(CN)_4$, belongs to the cubic crystal system and the neutron measurements made here give a unit cell edge of $a = 12{\cdot}529 \pm 0{\cdot}014$ Å. (Volume of unit cell $= 1967$ Å$^3$). There are 8 formula units in the unit cell and the observed systematic absences of neutron reflexions are consistent with the space group *Fd*3*m**. The linear absorption coefficient was determined experimentally in the diffractometer itself by measuring the transmission through a crystal plate of known thickness and found to be $0{\cdot}294$ cm$^{-1}$.

Single crystals were grown by slow evaporation from a saturated aqueous solution at room temperature. The crystals obtained were generally tabular, six-sided, the forms observed being {111}. Twinning is frequent on one of the (111) faces.

Zero-layer neutron-diffraction data were collected about the $[1\bar{1}0]$ axis at the CIR using the diffractometer described elsewhere (Chidambaram, Sequeira & Sikka, 1964*a*). In all, 96 *hhl* reflexions within the limit $\sin\theta/\lambda \le 0{\cdot}73$ ($\lambda = 1{\cdot}029$ Å) were examined using a cylindrical specimen of diameter 1·9 mm and length 5·7 mm (weight 26·3 mg). Complete diffraction profiles were recorded for 51 reflexions. For the remaining reflexions, which were very weak, only peak intensities ($I_p$) were measured and the integrated intensities ($I$) were calculated with the help of the ($I/I_p$) *versus* $2\theta$ correlation curve (Chidambaram, Sequeira & Sikka, 1964*b*) developed with the use of diffraction profiles of scanned reflexions. The intensities of 14 strong reflexions were also recorded with a smaller specimen of diameter 1·1 mm and length 5·0 mm (weight 7·3 mg) in order to estimate the effect of extinction. It may be mentioned here that preliminary measurements with a trial specimen did not show any increase in the diffracted intensity of strong reflexions after subjecting the crystal to thermal shocks by repeated dipping in liquid nitrogen. However, comparison of the integrated intensities obtained from the large and the small crystals showed that five of the strong reflexions from the former were affected by extinction. Hence, to start with, for these reflexions alone, intensities recorded from the smaller specimen were used after suitable normalization.

## Analysis and refinement of the structure

Preliminary estimates of the absolute intensity scale were obtained by comparing the observed intensities with the calculated $|F|^2$ values for some strong low-angle reflexions which remain practically constant with respect to the different models. The absorption was found to be small (about 5% for the larger specimen). An initial set of structure factors was calculated for all the four models based on information obtained from Dickinson's structure and using reasonable temperature factors. In the unit cell there are 8 Zn, 16K, 32C and 32N atoms, which occupy the following sets of equivalent positions (*International Tables for X-ray Crystallography*, 1952):

$$\begin{array}{rcl} 8\text{Zn in } 8(a) & - & \tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}; \ldots \\ 16\text{K in } 16(d) & - & \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}; \ldots \\ \left.\begin{array}{r} 32\text{C in } 32(e) \\ 32\text{N in } 32(e) \end{array}\right\} & - & u, u, u; \ldots \end{array}$$

The cyanide ions were taken to be centered at $u = 0{\cdot}245$ (Dickinson, 1922) and a C–N distance of 1·16 Å was assumed. The R values $[R = (\Sigma\, ||F_o| - |F_c||)/\Sigma\, |F_o|]$ of 0·520, 0·263, 0·318 and 0·268 were obtained for models I, II, III and IV respectively (see *e.g.* Sequeira (1965) for the structure factor expression for a freely-rotating cyanide ion).

A Fourier synthesis of the nuclear scattering density (the plane group for the projection is *cmm*) was

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* Space groups *Fd*3 and $F4_132$ are also consistent with the systematic absences. However, all the three space groups give the same equivalent positions for the atoms in the structure.

then made with the signs calculated for the static disordered model IV. The appearance of well-defined peaks in the projection (Fig. 1) as well as the very high $R$ index (including some serious discrepancies between $F_o$ and $F_c$ for low-angle reflexions) clearly eliminated model I (the dynamic model), which was dropped at this stage.

A diagonal-matrix least-squares refinement was first carried out on the basis of model II, using revised temperature factors indicated by the Fourier map and with a weighting scheme $w=4C_N^2/F_0^2(C_N+2C_B+0{\cdot}0001C_N^2)$ (Peterson & Levy, 1957; here $C_N$ is the net signal count and $C_B$ the background count). The structure factors calculated after this refinement showed further traces of extinction still present for the three strongest reflexions. Extinction corrections were now applied by treating extinction as variable absorption (Darwin, 1922) and using the data from the larger specimen for all reflexions except 222. For 222 alone, extinction was more than 30% and so the intensity obtained from the smaller crystal was used.

Structure factors were also calculated for models III and IV with positional parameters obtained from the above mentioned least-squares calculation, the temperature factors being suitably adjusted. The scale factors were independently adjusted and extinction corrections were applied separately for each model.

Each of the three models was then independently refined by six cycles of full-matrix least-squares calculations on a CDC 3600 computer. The parameters converged for all three models and the final $R$ values for the three models clearly indicate that model II is the correct one. The final parameters and the $R$ indices $R$ and $R_w$ $(=[\Sigma\, w||F_o|-|F_c||^2)/\Sigma\, w|F_o|^2]^{\frac{1}{2}})$ for all 3 models are listed in Table 1.

Table 1. $K_2Zn(CN)_4$: *Parameters and R indices for models* II, III *and* IV *obtained from isotropic least-squares analyses*

| Parameter | Model II (Zn–C) | Model III (Zn–N) | Model IV (Average) |
|---|---|---|---|
| $u_1$* | 0·2708 | 0·2720 | 0·2714 |
| $u_2$* | 0·2176 | 0·2201 | 0·2183 |
| $B_1$(Å$^2$) | 4·19 | 2·68 | 3·30 |
| $B_2$(Å$^2$) | 3·00 | 4·65 | 4·22 |
| $B_K$(Å$^2$) | 3·87 | 3·07 | 3·82 |
| $B_{Zn}$(Å$^2$) | 2·80 | 2·07 | 2·39 |
| $R$ | 0·138 | 0·224 | 0·189 |
| $R_w$ | 0·086 | 0·181 | 0·113 |

* Subscript 1 indicates N, C and (C+N)′/2 and subscript 2 indicates C, N, and (C+N)″/2 for models II, III and IV respectively.

### *Refinement using anisotropic thermal parameters*

A difference map calculated after the first cycle of least-squares refinement of model II showed considerable anisotropy in the thermal motions of the C, N and K atoms. Because of crystal symmetry these atoms have only two independent thermal vibration parameters, $B_\parallel$ and $B_\perp$ (analogous to the isotropic temperature factor $B$), respectively parallel and perpendicular to the threefold axis; Zn must have a single isotropic temperature factor. One cycle of full-matrix least-squares refinement* using anisotropic thermal parameters for C, N and K and an isotropic temperature factor for Zn, carried out at this stage with a desk calculator, improved the conventional and weighted $R$ indices ($R$ & $R_w$) to 0·103 and 0·059 (the accepted corrections to the parameters were 0·6 of the calculated shifts). All the coordinates and thermal parameters were then refined by six cycles of full-matrix least-squares refinement on the CDC 3600 computer. The final position coordinates and temperature factors, along with their standard deviations are given in Table 2, and the corresponding weighted and conventional $R$ values are 0·0567 and 0·0938 respectively. The observed and calculated structure factors are listed in Table 3.

### *Analysis of anisotropic thermal vibrations*

The anisotropic thermal parameters of C and N have been analysed in terms of rigid-body translational and

Table 2. $K_2Zn(CN)_4$: *final parameters from the anisotropic least-squares analysis**

| | $u$ | $B_\parallel$ | $B_\perp$ |
|---|---|---|---|
| N | 0·2712 ± 0·0002 | 2·62 ± 0·18 Å$^2$ | 4·74 ± 0·16 Å$^2$ |
| C | 0·2180 ± 0·0003 | 2·57 ± 0·21 | 3·26 ± 0·14 |
| K | 0·5000 | 2·24 ± 0·61 | 3·40 ± 0·78 |
| Zn | 0·1250 | 2·32 ± 0·02 | 2·32 ± 0·02 |

* $B_\parallel$ and $B_\perp$ are analogous to the isotropic temperature factor $B$ and correspond respectively to thermal motion parallel and perpendicular to the threefold axis.

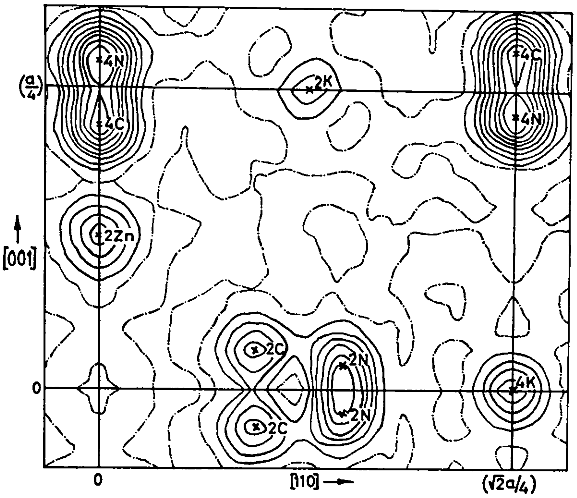

Fig. 1. Projection of the nuclear scattering density of $K_2Zn(CN)_4$ along [1$\bar{1}$0]. The contours are at intervals of 1·0 × $10^{-12}$ cmÅ$^{-2}$. The zero contour is a dot-dash line.

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* Each of the atoms N, C and K occurs in two sets of non-equivalent positions in the plane group *cmm* of the projection studied (Fig. 1). A special program was, therefore written for this problem where the structure factor and derivative expressions were explicitly written in terms of $u$, $B_\parallel$ and $B_\perp$.

Table 3. *Observed and calculated structure factors*

The nuclear scattering lengths used are (in units of $10^{-12}$ cm): potassium 0·35; zinc 0·61; carbon 0·66; nitrogen 0·94.

$|F_o|$ values derived from peak intensity measurements as described in the text are marked with asterisks.

| hhl | $\|F_o\|$ | $F_c$ | hhl | $\|F_o\|$ | $F_c$ | hhl | $\|F_o\|$ | $F_c$ | hhl | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 220 | 10.29 | 9.51 | 004 | 37.44 | 37.53 | 11,11,7 | 0* | -0.09 | 2,2,12 | 2.96* | -3.55 |
| 440 | 34.71 | 35.71 | 224 | 1.55* | -1.00 | 008 | 17.83 | 17.05 | 4,4,12 | 5.08 | -4.08 |
| 660 | 25.70 | 25.54 | 444 | 21.10 | 19.36 | 228 | 4.51 | 4.61 | 6,6,12 | 5.05 | -5.71 |
| 880 | 6.68 | 7.24 | 664 | 12.97 | 12.27 | 448 | 11.56 | 11.27 | 8,8,12 | 2.19* | -1.16 |
| 10,10,0 | 15.66 | 16.51 | 884 | 0.94* | 0.48 | 668 | 7.04 | 6.90 | 1,1,13 | 6.65 | -7.23 |
| 12,12,0 | 3.33 | 4.25 | 10,10,4 | 7.65 | 8.04 | 888 | 3.75* | 4.08 | 3,3,13 | 1.52* | -1.73 |
| 111 | 1.16 | 0.92 | 12,12,4 | 1.54* | 0.36 | 10,10,8 | 3.23* | 4.32 | 5,5,13 | 5.94 | -6.61 |
| 331 | 1.31* | 1.63 | 115 | 6.56 | -6.31 | 119 | 2.32* | -2.37 | 7,7,13 | 2.19* | -3.01 |
| 551 | 2.27 | -2.58 | 335 | 0.91* | -2.45 | 339 | 4.52 | 3.76 | 9,9,13 | 0* | 0.05 |
| 771 | 7.74 | 7.36 | 555 | 8.23 | -7.90 | 559 | 3.71 | -3.68 | 2,2,14 | 11.23 | 10.90 |
| 991 | 5.79 | -5.48 | 775 | 2.99* | 2.00 | 779 | 3.67* | 2.93 | 4,4,14 | 3.07* | 2.95 |
| 11,11,1 | 5.23 | 5.11 | 995 | 4.72 | -5.35 | 999 | 1.96* | 1.33 | 6,6,14 | 3.78* | 3.97 |
| 222 | 34.55 | -35.18 | 11,11,5 | 1.77* | 0.68 | 11,11,9 | 1.71* | -0.29 | 8,8,14 | 3.41 | 4.02 |
| 442 | 14.88 | -13.94 | 226 | 16.34 | -15.02 | 2,2,10 | 5.44 | 4.98 | 1,1,15 | 1.90* | 2.07 |
| 662 | 5.46 | -5.29 | 446 | 7.76 | -6.91 | 4,4,10 | 0* | 0.36 | 3,3,15 | 5.14 | 5.54 |
| 882 | 20.09 | -19.82 | 666 | 1.54* | -0.65 | 6,6,10 | 3.37* | 3.50 | 5,5,15 | 0* | 0.61 |
| 10,10,2 | 2.13* | 2.49 | 886 | 9.40 | -9.86 | 8,8,10 | 1.90* | 0.39 | 7,7,15 | 1.58* | 1.51 |
| 12,12,2 | 6.41 | -6.74 | 10,10,6 | 1.94* | 2.50 | 10,10,10 | 2.95* | 2.13 | 0,0,16 | 6.18 | -5.86 |
| 113 | 7.75 | -6.45 | 12,12,6 | 2.48* | -3.41 | 1,1,11 | 3.72* | -3.49 | 2,2,16 | 0* | 0.94 |
| 333 | 5.82 | -4.45 | 117 | 0.24* | -0.20 | 3,3,11 | 2.33* | 2.44 | 4,4,16 | 1.65* | -1.78 |
| 553 | 10.21 | -9.40 | 337 | 4.36 | 4.56 | 5,5,11 | 6.31 | -5.69 | 6,6,16 | 2.43* | -2.58 |
| 773 | 2.64* | 1.16 | 557 | 5.49 | -4.12 | 7,7,11 | 0* | -0.72 | 1,1,17 | 2.45* | -2.71 |
| 993 | 9.44 | -9.43 | 777 | 3.77 | 3.71 | 9,9,11 | 0* | -0.82 | 3,3,17 | 1.05* | -0.38 |
| 11,11,3 | 1.58* | 0.55 | 997 | 2.90* | -2.27 | 0,0,12 | 8.91 | -8.23 | 2,2,18 | 6.40 | 6.84 |

rotational vibrations of the cyanide ion following Cruickshank (1956*a*). From an examination of the thermal parameters of C and N (Table 2), it is clear that the N atom has a much larger amplitude of thermal vibration perpendicular to the C–N bond as compared with the C atom. Hence, the cyanide ion as a whole may be reasonably assumed to perform angular oscillations around Zn as centre. If these motions of the cyanide ion are to satisfy the symmetry of the crystal, there need be only three independent thermal parameters to describe them, these parameters being

$T_{11}$ Mean-square amplitude of translation along the C–N bond, *i.e.* along the threefold axis.

$T_{33}$ Mean-square amplitude of translation along the perpendicular to the C–N bond.

$\omega_{33}$ Mean-square angle of oscillation around axes perpendicular to the C–N bond and passing through Zn.

These parameters have been evaluated from the mean-square thermal displacements of C and N, and the values are

$$T_{11} = 0{\cdot}0329\ \text{Å}^2$$
$$T_{33} = 0{\cdot}0286\ \text{Å}^2$$
$$\omega_{33} = 10{\cdot}24\ \text{deg}^2\ .$$

Using the above value of $\omega_{33}$, the radial errors in the Zn–C and Zn–N distances and hence in the C–N bond length have been estimated following Cruickshank (1956*b*). The final bond lengths with correction for anisotropic motion and the bond angles are given in Table 4.

Table 4. *Interatomic distances and bond angles in* $K_2ZN(CN)_4$

| | Uncorrected for thermal motion | Corrected for thermal motion |
|---|---|---|
| Zn–C | 2·018 ± 0·007 Å | 2·024 ± 0·007 Å |
| K–N | 2·891 ± 0·007 | — |
| C–N | 1·155 ± 0·009 | 1·157 ± 0·009 |
| K–N–C | 117°48′ ± 27′ | — |
| N–K–N | 79 01 ± 9<br>100 59 ± 9 | |
| Cu–Z–N | 180 00 | |

## Discussion and conclusions

The appearance of clear and well-defined peaks in the Fourier map, the very high *R* value and some serious low-angle discrepancies between the observed and calculated structure factors easily ruled out the dynamic model (model I) at the early stages of the analysis. The correctness of model III was also in doubt as it gave some low angle discrepancies. It is of interest to note that the signs of the structure factors calculated on the basis of models II, III and IV are all the same and hence the projection of the nuclear scattering density (Fig. 1) does not depend on any further structural assumptions. In the projection, the N atom peak appears slightly stronger and broader compared with the C atom peak. This does not seem to favour models III and IV. The absence of any spurious peaks in the difference Fourier synthesis carried out on the basis of model II also showed that this model cannot be basically wrong.

However, the most conclusive results were obtained from the least-squares refinement. In six cycles of least-squares refinement using isotropic temperature factors, the parameters had fully converged for all the three models and final weighted *R* values of 0·086, 0·181 and 0·113 were obtained for models II, III and IV respectively. This clearly shows that model II, with the cyanide ion having a coordination of the type –Zn–C–N–K–N–C–Zn– is the correct model.

The least-squares refinement further shows that in models III and IV the 'inner' (*i.e.* closer to Zn) atom vibrates more than the 'outer' atom. This is rather unreasonable and therefore also supports the conclusion that model II is the correct model.

It may be mentioned here that the isotropic and the anisotropic models give weighted *R* values of 0·0864 and 0·0567 respectively resulting in a *R* index ratio of 1·523, which is very much greater than the value of $R_{3,46,0\cdot005} = 1{\cdot}154$ (Hamilton, 1965) for the significance level of 99·5%*. This shows that the anisotropy is highly significant. Zinc has the usual tetrahedral coordination while potassium is surrounded by six nitrogen atoms which form a trigonal antiprism around it. The Zn–C distance of 2·024 Å is close to the sum (2·00 Å) of the tetrahedral covalent radius of the zinc atom, 1·31 Å (Pauling, 1960), and the covalent radius of the *sp*-hybridized carbon atom, 0·69 Å (Bent†, 1961). In $K_3Co(CN)_6$ (Curry & Runciman, 1959) also, the experimental Co–C distance of 1·89 Å compares well with the sum (1·91 Å) of the covalent radii of the cor-

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* Note that 38 of the weak reflexions, whose intensities were estimated from peak-intensity measurements, were given zero weight in the refinement.

† The authors are grateful to the referee for bringing this reference to their notice.

responding atoms. The K–N distance of 2·89 Å is comparable to the value of 2·78 Å (mean of three distances: 2·70, 2·79, 2·83) found in $KAu(CN)_2$ (Rosenzweig & Cromer, 1959). The C–N distance of 1·157 Å (corrected for thermal motion) is also in good agreement with the C–N distance found in other cyanides – 1·15 Å in $K_3Co(CN)_6$, 1·15 Å in $As(CN)_3$ (Emerson & Britton, 1963), 1·15 Å in $P(CN)_3$ (Emerson & Britton, 1964) and 1·17 Å in $KAu(CN)_2$.

We are very grateful to Dr G. S. Rao of the Chemistry Division for the preparation of the substance. The isotropic and anisotropic structure-factor least-squares calculations were carried out on the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay, with programs written by Dr S. Srikanta. The assistance of Shri S. K. Sikka and Shri S. N. Momin in recording some of the data is gratefully acknowledged.

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# Optical and Interferometric Studies on Thermal Etch Patterns of Potassium Chloride Cleavages

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Freshly cleaved potassium chloride has been thermally etched at temperatures near to its melting point. It is observed that the thermal etch patterns produced consist of (1) circularly terraced and (2) spiral etch pits. The topography of the thermally etched face and of the thermal etch pits is studied by multiple-beam interference fringes. Dissociation of circular terraces of the etch pits into two branches has been observed. It is shown by a schematic diagram that this may be due to the interference of circular terraces of etch pits originating at two dislocations very near to each other. The interference of a number of circular terraced pits is recorded. It is observed that some of the etch pits have a spiral structure for a few turns and then the terraces become concentric circles. The formation of spiral pits as well as pits having closed rings has been assumed to be due to the mechanism of the etching process as reported by Lang and has nothing to do with screw dislocations.

## Introduction

It is well known that when crystals are heated to a temperature very near to their melting point, thermal etch pits, similar to the etch pits produced by chemical etching, are produced at the sites of dislocations. The dislocation theory of evaporation has been given by Cabrera & Levine (1956). The correlation between the thermal etch pits and the dislocations has been reported by Hirth & Vassamillet (1958). Patel, Bahl & Vagh (1965) have established for the first time one to one correspondence in the number and position of etch pits on matched faces of sodium chloride by etching one face chemically and the other thermally, indicating thereby that the pit formations originate from the crystal defects known as dislocations. Etch spirals pro-