STRUCTURAL AND MAGNETIC TRANSITIONS IN K_2ReCl_6

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ABSTRACT

The five different structures of K_2ReCl_6 have been refined by the Rietveld technique from high resolution neutron powder data. At room temperature the structure is cubic Fm3m; at 111K, an alternate rotation of $ReCl_6$ octahedra around the c-axis produces the tetragonal ($00c^-$) C4/mcn phase; at 103K a rotation of all octahedra around the b-axis produces the shear of the monoclinic ($0b^+c^-$) C2/c phase; at 76K, an equivalent rotation around the remaining $\bar{a}$-axis, with a net shear around ($\bar{1}10$) reduces the symmetry to ($b^+b^+c^-$) $P2_1/n$; finally at 11.9K, the Re moments align antiferromagnetically in alternate c-planes, echoing the $ReCl_6$ anti-tilt pattern around the c-axis. In K_2SnCl_5, Boysen and Hewat (1978) found the same sequence, but with the second and third transitions occuring simultaneously. These structures are in accord with recent inelastic scattering results and group theoretical considerations and, if extended to include a hypothetical triclinic ($a^+b^+c^-$) $P\bar{1}$ phase, probably describe all known phases of K_2PtCl_6 type compounds.

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1. INTRODUCTION

K_2ReCl_6 has been of interest because it appeared to offer the possibility of studying the distribution of magnetic moment of the 5d electrons on the Re^{4+} ion in a simple face-centred cubic lattice. However, the earliest neutron diffraction measurements on this material (Smith and Bacon, 1966) revealed structural changes at low temperature. The lowest temperature structure was said to be primitive cubic, which is possible with a tilting of the $ReCl_6$ octahedra so as to destroy the face-centering equivalence; this would be analogous to the cubic Im3 distorted-perovskite structure proposed by Glazer (1972). Of course, in K_2PtCl_6 type structures the octahedra are not connected as in perovskite and the sequence of possible space groups is quite different; the cubic low temperature phase would then be Pn3 rather than Im3.

Busey, Dearman and Bevan (1962) have found sharp anamolies in the specific heat of K_2ReCl_6 at 111K, 103K and 76K, in addition to that due to the antiferromagnetic ordering at 11.9K. O'Leary and Wheeler (1970) reported an extensive study of the lattice dynamics and phase transitions in the material and concluded that the Fm3m room temperature structure probably transformed to a cubic Pn3 low-temperature structure via three distinct transitions:

$$Fm3m \xrightarrow{111K} I4/m \xrightarrow{103K} P4_2/n \xrightarrow{76K} Pn3$$

Van Driel, Armstrong and McEnnan (1975) supported such a view with NQR evidence for a softening of the zone-centre, $ReCl_6$ rotary mode frequency. Lynn, Patterson, Shirane and Wheeler (1978) have confirmed the simultaneous softening of these modes using inelastic neutron scattering: the $ReCl_6$ rotational mode first condenses at the zone centre Γ (corresponding to out-of-phase rotations of $ReCl_6$ octahedra) and then at the zone boundary X (corresponding to in-phase rotations).

wrong way round

Boysen and Hewat (1978) have, however, shown that the series of transitions in the isomorphous K_2SnCl_6 is quite different to that proposed by O'Leary and Wheeler for K_2ReCl_6, the symmetry being reduced with temperature to become finally monoclinic:

$$Fm3m \xrightarrow{261K} P4/mnc \xrightarrow{255K} P2_1/n$$

This sequence also appears to be in agreement with the inelastic scattering results for K_2SnCl_6. It would be interesting therefore if a different sequence, such as that proposed by O'Leary and Wheeler (1970) could be verified by quantitative crystallographic measurements on K_2ReCl_6, and especially if the proposed transition from tetragonal $P4_2/n$ to cubic Pn3 at lower temperature could be confirmed.

Henkel, Petzl, Höck and Thomas (1980) have used Landau's theory of phase transitions to obtain the only possible sub-groups for a single transition from Fm3m consistent with condensation ~~the inelastic scattering results~~. They conclude that, for a second-order transition, only tetragonal P4/mnc (or C4/mnc) and cubic Pn3 are possible. (Other groups are possible for a first order transition involving more than one soft mode).

Brown (1964) has discussed the possible transitions in K_2XCl_6 structures from simple packing arguments, without the benefit of ~~the~~ lattice dymnamics. He has shown that if the K^+ ion is more than 2% smaller than the cavity available to it, then one can expect a distortion from the ideal cubic structure, at least at low temperature. The dozen examples he gives indicate that the symmetry in such cases will be less than cubic and even triclinic in the case of K_2TeI_6, where the cavities available for K^+ are particularly large. Indeed, there are rather few A_2XCl_6 structures, apart from K_2PtCl_6 itself, where the A^+ cation fits the cavity to within 2% and we can therefore regard this cubic structure as, at best, an idealized or high-temperature form.

The only conclusive way of deciding on the sequence of transitions for a particular material is to obtain high resolution crystal structures for each of the phases; inelastic scattering measurements and group theoretical arguments can only indicate what types of structure are possible. Such crystallographic measurements are difficult, if not impossible, with conventional single crystal techniques because of the inevitable and complex twinning in the lower symmetry phases. Rietveld profile analysis of high resolution neutron powder patterns has, however, proved particularly effective for the crystallographic study of such phase transitions (Hewat,1973b). In this paper we report analyses of the five different structures of K_2ReCl_6. A detailed knowledge of the crystallographic parameters of the $P2_1/n$ phase are a necessary adjunct to polarized neutron diffraction measurements of the spatial distribution of the aligned paramagnetism at 20K. They enable the observed flipping ratios to be converted to magnetic structure factors, which themselves carry direct information on the covalency in this 5d transition metal salt. The polarized neutron study will be reported elswhere (Forsyth, Brown and Wedgwood,1981).

2. EXPERIMENTAL

A sample of powdered K_2ReCl_6 was supplied by Messrs. Johnson Matthey Chemicals Limited, Royston, England. It was prepared using the method described by Brauer (1965) and originated by W. Gielmann, namely the reaction between rhenium metal and potassium chloride, heated to 300°C, first under N_2 then under a slow stream of Cl_2. A spectroscopic examination showed detectable calcium and silver impurities at 5 and 2 parts per million by weight respectively. An X-ray powder photograph, taken at ambient temperature with Cu Kα radiation and a 57.3 mm radius Philips camera, showed only lines which could be indexed on a cubic unit cell with a = 9.78Å.

The powdered K_2ReCl_6 was firmly pressed into a 16 mm diameter vanadium container and aligned in a standard He gas-flow cryostat in the 15 mm high D1A neutron beam (Hewat and Bailey,1976). The absorption, measured to be $\mu R = 0.87\ cm^{-1}$, was used to correct the overal Debye-Waller factor by $\Delta B = 0.57$ at the end of each refinement (Hewat 1979). In order to clearly resolve possible line splitting and superlattice reflections, a wavelength of 1.909 Å was chosen, giving $\sin \theta/\lambda = 0.5 Å^{-1}$ at the maximum $2\theta = 161^{\circ}$. Complete diffraction patterns at steps of 0.05° 2θ were collected at 125K, 107K, 90K, 30K and 5K, taking 22 hours per run (about 37 seconds per point for a constant monitor count of 50 000). When the ten counters were averaged the statistical errors became very small, as is clear from figure 1., which shows a part only of each scan. It is immediately clear from these diffraction patterns that K_2ReCl_6 is certainly not cubic at low temperature, and that the symmetry decreases with decreasing temperature. Of course, neutron powder measurements at low temperature have already been made by Smith and Bacon (1966) and Minkiewiez, Shirane, Frazer, Wheeler and Dorain (1968) without any evidence of line splitting or broadening. It is only because our instrumental resolution is so much higher that we are able to observe small deviations from cubic symmetry. Detailed examination of these splittings and the line symmetries due to unresolved splittings produced models for refinement. The changes in the lattic constants and the appearance of certain groups of superlattice reflections can be interpreted using the techniques Glazer (1972) developed for distorted perovskites. However, such models must then be tested by refinement to account for the entire diffraction pattern. Such excellent fits were obtained for the different phases of K_2ReCl_6 that it is difficult to believe that we have not obtained the correct structures, especially since the sequence of transitions can be understood in an extremely simple way which is also consistent with the inelastic scattering results.

The interactive POWDER programs (Hewat 1978) and the Rietveld profile refinement programs (Hewat 1973a) were used to analyse the different phases.

3. THE DIFFERENT PHASES OF K_2ReCl_6

The space group and its equivalent positions, the atomic positional and thermal parameters and the Re-Cl bond lengths and angles for the five phases of K_2ReCl_6 are given in Tables 1, 2 and 3 respectively.

i) Fm3m (125K)

The cubic K_2PtCl_6 structure can best be described as a cubic close packing of large octahedral $PtCl_6^{2-}$ ions, with the K^+ ions occupying the tetrahedral holes between them (fig. 1XC,10, Wyckoff, 1965). All atoms are in special symmetry positions and the only co-ordinate parameter reflects the distance along the cube axis between the Re and Cl atoms. In addition, it is necessary to allow anisotropic Debye-Waller factors for the Cl atoms in order to accoumt for the strong libration of the $ReCl_6$ ions.

ii) C4/mcn (107K)

The line splitting at 107K, only just below the 111K transition, is too small to be completely resolved, but the appearance of superlattice reflections and line broadening characterizes the new structure. For example, the cubic (800) reflection at $2\Theta = 102^\circ$ appears to contain a low angle wing of about half the intensity of the higher angle component. This indicates a tetragonal cell with $a = b < c$, which is to be expected for a single tilt of the $ReCl_6$ octadedra around the c-axis, shortening both a and b.

In the C4/mcn setting the Fm3m axes are retained, but all the $ReCl_6$ ions in one (001) plane are tilted in the same direction to reduce the size of the too large hole available to K^+ (fig. 3). The C-centering is therefore retained, but the $ReCl_6^{2-}$ octahedra in the next layer are tilted in the opposite sense, destroying the centering on the other faces and producing the superlattice reflections seen in the diffraction pattern. The weak intensities of these superlattice reflections, and hence the tilt angle, are well determined because of the good statistics obtaine by averaging the ten counters. This $(00c^-)$ tilting mode reduces the size of the K+

hole a little more than the alternative ($00c^+$) mode, in which all layers would be tilted in the same sense. The only co-ordinate parameters reflect the Re-Cl distance and tilt angle, but again anisotropic Debye-Waller factors are needed for the chlorine atoms to describe the remaining librations of the $ReCl_6$ ion.

The standard description of the new cell, P4/mcn, as used for K_2SnCl_6 (Boysen and Hewat, 1978) is obtained by rotating the (x,y) axes by 45°. However, the C-face centred cell is best retained for continuity between Fm3m and the next phase, C2/c.

iii) C2/c (90K)

This phase is not found in K_2SnCl_6, and at first presented some difficulty. At the second transition the splitting also appeared to be tetragonal, as reported by O'Leary and Wheeler (1970), but now with $a = b > c$ instead of $a = b < c$. (See for example the original (800) line at $2\theta = 103^\circ$, which again appears to be split into two components, but now with twice the intensity in the lower-angle part). However, it was then realised that such a psuedo-tetragonality $a < b = c$ is characteristic of a ($0\ b\ c^-$) tilting if the two tilts are nearly equal: the first ($00c^-$) tilt shortens the a and b axes, while the second (0 b 0) tilt shortens a and c. The absence of the necessary additional superlattice reflections rules out a ($0\ b^-\ 0$) tilt, so the tilt pattern can only be ($0\ b^+\ c^-$).

On the same axes (fig 3), the $ReCl_6$ octahedra are therefore all tilted by the same angle around [010]. The C-centering is retained, but the whole structure is sheared around this axis so that the angle between [100] and [001] is no longer 90°: the structure must be monoclinic with unique axis b. The only space group which also contains a glide plane along c due to the alternating tilts about this axis is C2/c. In addition to the chlorine co-ordinate paramete describing the Re-Cl distances and tilts, there are now two different K^+ ions which are permitted in this space group to move along [100]. The refinement indicates that these displacements are equal, within the calculated error limits, and in opposite directions.

iv) $P2_1/n$ (30K)

The diffraction pattern now becomes very complex, but some characteristic features can still be identified. For example, the (008) component at $2\theta = 103^\circ$ remains, but the former (800) satellite dramatically changes sides, and we can now identify this reflection as (440) on new (x,y) axes rotated by 45°. The entire pattern can be explained by another equivalent (b^+ 00) rotation of all $ReCl_6$ octahedra about the remaining [100] axis, with a corresponding shear of the structure about this axis. If the (b^+00) and (0 b^+ 0) tilts are equal, the resultant shear is about the original [110] direction, which becomes the new b-axis of a primitive cell based on the equivalent (000) and (½ ½ 0) positions of C2/c. Of course, the glide plane due to the alternate tilts around the c-axis is retained and the space group is therefore $P2_1/c$, or $P2_1/n$ with our choice of axes.

It is interesting to note that if this last tilt was not equal to the preceding one, the resultant shear could not be resolved along a single lattice direction. The result would therefore be a triclinic $P\bar{1}$ cell and an even more complex diffraction pattern. Brown (1964) has found that K_2TeI_6, for which the hole available for K^+ is particularly large, has a triclinic cell at room temperature. We suppose that this is due to unequal tilts, ie. ($a^+ b^+ c^-$), instead of ($b^+ b^+ c^-$) as in K_2ReCl_6 and K_2SnCl_6 In fact, we can think of no physical reason why the successive tilts in K_2ReCl_6 should necessarily be equal; our monoclinic cell may be only an approximation, even though a very good one, to the "true"$P\bar{1}$ structure of K_2ReCl_6. $P2_1/n$ may, however, be exact for K_2SnCl_6, where the last two tilts appear to condense simultaneously (Boysen and Hewat, 1978).

In addition to the Re-Cl distances and tilt parameters, there appears to be some significant displacement of the K^+ ion from its original position. However, in all of these centrosymmetric structures the Re^{4+} ion is strictly fixed at the centre of its $ReCl_6$ octahedron. The excellent fits obtained for the data, especially for this very complex low temperature pattern, convince us that we have very good descriptions of the structures without lowering the symmetry still further.

v) $P2_1/n$ (5K) antiferromagnetic structure

The only apparent change in the diffraction pattern is the appearance of five additional weak reflections between $2\theta = 10^\circ$ and 35° (Fig. 2), due to the antiferromagnetic ordering originally reported by Smith and Bacon (1966). According to these and later authors, the spins of the 5d electrons on Re^{4+} are all aligned in the same direction in one of the original cubic planes and in the opposite direction in the adjacent plane. This is the same kind of ordering as the $ReCl_6^{2-}$ ($00c^-$) tilts. For the purposes of our model, we therefore assumed that the moments were aligned in the $\langle 110 \rangle$ directions of Re-Cl bonds. This simple model, together with the $P2_1/n$ atomic structure obtained at 30K, gives an excellent fit to all of the data at 5K. The magnitude of the moment is found to be $2.5 \pm 0.3\mu\beta$. In fact, the resolution of our diffractometer in this low angle region is still not sufficient to show the monoclinic splitting of the magnetic reflections, so we can not determine the absolute spin directions within the a-b plane and our data are also relatively insensitive to small angular displacements of the spins from this plane. These difficulties are compounded by the rapid fall off with sin θ/λ of the magnetic form factor for the rather diffuse 5d electrons, but might be resolved by using the longest available wavelength (5.7Å) to move the magnetic lines to higher angles where the resolution is better.

4. CONCLUSIONS

Our results clearly show that the lowest temperature phase of K_2ReCl_6 is not cubic Pn3, as had previously been thought, but monoclinic $P2_1/n$ as Boysen and Hewat (1978) have recently found for K_2SnCl_6. The sequence of transitions,

$$Fm3m \xrightarrow{111K} C4/mcn \xrightarrow{103K} C2/c \xrightarrow{76K} P2_1/n \xrightarrow{11.9K} P2_1/n$$

although quite different to that assumed until now, is in agreement with recent inelastic neutron scattering results, which show a condensation of the soft $ReCl_6$ rotational mode, (first at the zone centre Γ and then at the zone boundary X.) Furthermore, the sequence is the same as in K_2SnCl_6, except that there is now an intermediate phase, C2/c, which is not found in this latter material. This intermediate phase is due to the separate condensation of equal $(0\ b^+\ 0)$ and $(b^+\ 0\ 0)$ rotational modes, which condense at the same temperature in K_2SnCl_6. We conclude that K_2SnCl_6 should then be strictly monoclinic, $P2_1/n$, but that K_2ReCl_6 may be strictly triclinic $P\bar{1}$, and only monoclinic $P2_1/n$ to a good approximation. In any case, a triclinic example of this structural type, K_2TeI_6, is known.

Thus, far from having simple cubic structures, K_2PtCl_6 compounds tend to become triclinic at low temperature, with no symmetry apart from perhaps a centre. This collapse of a highly symmetric structure is simply due to the fact that the K^+ ion is generally too small for the hole available to it. The occurence of structures in which there is a small mismatch of ionic radii must be the rule rather than the exception in nature: it is likely then that many other materials will be found to exhibit similar phase transitions below ambient temperature.

The observed antiferromagnetic moment of 2.5 ± 0.3 μβ is lower than that to be expected for a Re^{4+} free ion ($S = 3/_2$). However, it is in agreement with the work of Smith and Bacon (1966) and Minkiewicz et al (1968), who found 2.6 ± 0.5μβ and 2.7 ± 0.3μβ respectively. The difference between the experimental values and the free ion form factor undoubtedly reflects the delocalization of the magnetization due to covalency, but our data are too sparse and unresolved to support a more detailed analysis.

FIGURE CAPTIONS

Figure 1 Observed and calculated neutron powder diffraction profiles for $K_2ReC\ell_6$ at (a) 125K, (b) 107K, (c) 90K and (d) 30K. The complete profiles, on which the refinements were made, extend from 0° to 161° 2θ, and are averaged over all ten counters. Of particular interest are the different splittings of the cubic (800) reflection at about $2\theta = 103°$; these are well explained by the simple sequence of transitions proposed in this paper, which require the symmetry at 90K to be only pseudo-tetragonal, and not tetragonal as indicated at first sight.

Figure 2 Observed and calculated diffraction profiles at 5K showing five weak antiferromagnetic lines between $2\theta = 10°$ and 35° : these lines are well explained by opposing Re^{4+} spins on alternate [001] planes, echoing the alternate $[00c^-]$ octahedral tilts around this axis. Since the monoclinic splitting cannot be resolved at such low angles we have, however, no experimental evidence for the absolute spin directions.

Figure 3 The $[00c^-]$ tilt pattern in the (x,y) plane at the first transition, showing opposing tilts in alternate planes along [001]. The next two transitions produce in-phase tilts, first about [010] and then about [100]. Since these latter tilts are equal, at least to a very good approximation, the final structure is $[b^+b^+c^-]$ monoclinic ($P2_1/n$) rather than $[a^+b^+c^-]$ triclinic ($P\bar{1}$).

CAPTIONS

Table 1 — Symmetry equivalent positions for the different settings of the space groups. The original Fm3m axes have been retained for all settings except $P2_1/n$, where the (x,y) axes have been rotated by 45° to avoid the use of the triclinic cell which would be needed if the $[a^+00]$ and $[0b^+0]$ hits were not equivalent. An attempt has been made to show which equivalent positions are retained at each transition, and which are lost.

Table 2 — Structural parameters obtained by profile refinement at each temperature, with scattering lengths $b_K = 0.35$, $b_{Re} = 0.95$ and $b_{C\ell} = 0.958$ (10^{-12}cm). Anisotropic temperature factors have been refined for the chlorine atoms to account for the strong librations of the $ReC\ell_6$ octahedra. (Large chlorine B-factors perpendicular to the Re-Cℓ bonds). In the low temperature $P2_1/n$ phase, such librations were no longer evident, since all of the tilts had condensed, and isotropic B-factors were therefore used to reduce the number of parameters. The R-factor for integrated intensities $R_I = 2R_F$, the usual R-factor for structure factors, shows that very good fits were obtained, especially for the highest and lowest symmetry phases.

Table 3 — Re-Cℓ bond lengths and angles show that the $ReC\ell_6$ octahedra are quite regular, especially in the lowest (and highest) temperature phases.

Table 1

Fm3m	C4/mnc mcn	C2/c	$P2_1/n$
$\boxed{A}$ (xyz) (yzx) etc. (yxz) etc. $(\bar{x}\bar{y}z)$ $(\bar{y}z\bar{x})$ etc. $(\bar{y}\bar{x}z)$ etc. $(\bar{y}xz)$ $(xz\bar{y})$ etc. $(x\bar{y}z)$ etc. $(y\bar{x}z)$ $(\bar{x}zy)$ etc. $(\bar{x}yz)$ etc. $\boxed{B}=\boxed{A} + (0\ \frac{1}{2}\ \frac{1}{2})$ (xyz) etc. $+ (0\ \frac{1}{2}\ \frac{1}{2})$ $(\bar{x}yz)$ etc. $+ (0\ \frac{1}{2}\ \frac{1}{2})$ (yxz) etc. $+ (0\ \frac{1}{2}\ \frac{1}{2})$ $(\bar{y}\bar{x}z)$ etc. $+ (0\ \frac{1}{2}\ \frac{1}{2})$ $\boxed{A} + (\frac{1}{2}\ \frac{1}{2}\ 0)$ $\boxed{B} + (\frac{1}{2}\ \frac{1}{2}\ 0) = \boxed{A} + (\frac{1}{2}\ 0\ \frac{1}{2})$	$\boxed{A}$ (xyz) $(\bar{x}\bar{y}z)$ $(\bar{y}xz)$ $(y\bar{x}z)$ $\boxed{B}$ $(x\bar{y}z) + (0\ \frac{1}{2}\ \frac{1}{2})$ $(\bar{x}yz) + (0\ \frac{1}{2}\ \frac{1}{2})$ $(yxz) + (0\ \frac{1}{2}\ \frac{1}{2})$ $(\bar{y}\bar{x}z) + (0\ \frac{1}{2}\ \frac{1}{2})$ $\boxed{A} + (\frac{1}{2}\ \frac{1}{2}\ 0)$ $\boxed{B} + (\frac{1}{2}\ \frac{1}{2}\ 0)$	$\boxed{A}$ (xyz) $\boxed{B}$ $(x\bar{y}z) + (0\ \frac{1}{2}\ \frac{1}{2})$ $\boxed{A} + (\frac{1}{2}\ \frac{1}{2}\ 0)$ $\boxed{B} + (\frac{1}{2}\ \frac{1}{2}\ 0)$	$\boxed{A}$ (xyz) $\boxed{B}$ $(x\bar{y}z) + (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$
Notes : Fm3m is the standard setting (International Tables, 1972)	C4/mnc is obtained from P4/mnc by $X = \frac{x-y}{2}$ $Y = \frac{x+y}{2}$	C2/c is obtained from the standard setting by rotation $X = z + x$ $Y = z - x$	$P2_1/n$ is obtained from $P2_1/c$ by rotation $X = z + x$ $Y = z - x$

mcn? yes

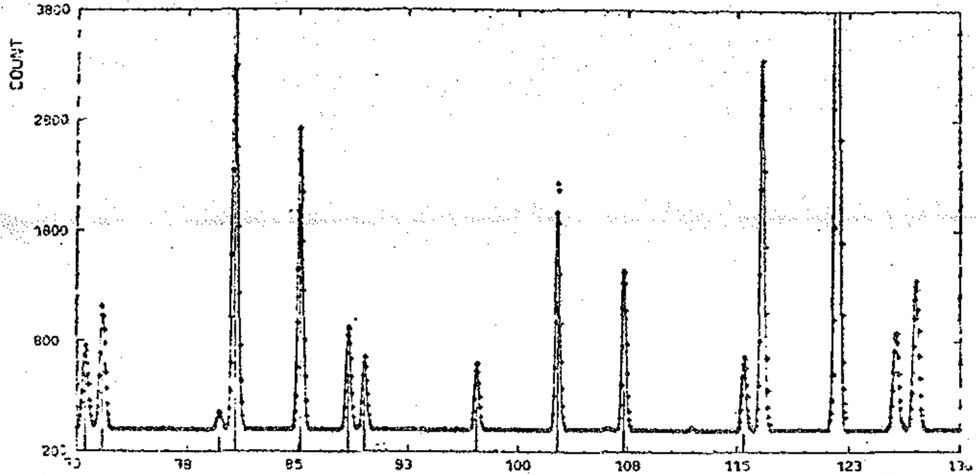
	125 K (Fm3m)	107K (C4/mnc)	90K (C2/c)	30K ($P2_1/n$)	5K ($P2_1/n$
K_x	0.25	0.25	0.25	0.5032 (22)	0.5054 (1
K_y	0.25	0.25	0.2392 (21) -0.2560 (23)	0.0097 (18)	0.0079 (1
K_z	0.25 $\bar{4}3m$ (8c)	0.25 222 (8d)	0.25 (mm2) 2× (8e)	0.2481 (26)	0.2552 (2
Re_x	0.	0.	0.	0.	0.
Re_y	0.	0.	0.	0.	0.
Re_z	0. m3m (4a)	0. 4/m (4a)	0. $\bar{1}$ (4a)	0.	0.
$Cl1_x$	0.2399 (11)	0.2375 (2)	0.2400 (4)	0.2621 (5)	0.2612 (4)
$Cl1_y$	0.	0.0051 (4)	0.0117 (4)	0.2181 (4)	0.2187 (4)
$Cl1_z$	0. 4mm (24e)	0. (16h)	-0.0147 (7) (8f)	-0.0180 (3)	-0.0175 (3)
$Cl2_x$	0.	-0.0051	-0.0122 (5)	0.2264 (5)	0.2248 (4)
$Cl2_y$	0.2399	0.2371 5?	0.2388 (4)	-0.2579 (4)	-0.2583 (4)
$Cl2_z$	0.	0.	-0.0035 (8) (8f)	-0.0098 (4)	-0.0100 (4)
$Cl3_x$	0.	0.	0.0140 (7)	0.0249 (4)	0.0256 (4)
$Cl3_y$	0.	0.	-0.0022 (8)	-0.0003 (7)	-0.0011 (7)
$Cl3_z$	0.2399	0.2433 (3) (8e)	0.2422 (5) (8f)	0.2415 (3)	0.2408 (3)
B(K)	1.28 (8)	0.85 (6)	0.87 (10)	0.91 (9)	0.63 (10)
B(Re)	0.42 (5)	0.10 (4)	0.43 (4)	0.39 (5)	0.20 (4)
B(Cl1)	0.39 (5)	0.65 (7)	0.79 (10)	0.33 (7)	0.26 (6)
	2.07 (4)	2.61 (19)	0.96 (23)	0.33	0.26
	2.07	1.63 (10)	1.56 (22)	0.33	0.26
	0.	0.84 (20)	0.09 (19)	0.	0.
	0.	0.	1.01 (24)	0.	0.
	0.	0.	0.31 (16)	0.	0.
B(Cl2)	2.07	2.61	2.74 (27)	0.66 (7)	0.31 (6)
	0.39	0.65	0.20 (13)	0.66	0.31
	2.07	1.63	0.14 (22)	0.66	0.31
	0.	0.84	0.15 (17)	0.	0.
	0.	0.	1.52 (27)	0.	0.
	0.	0.	0.16 (21)	0.	0.

@ 300 K $a = 9.83\overset{4}{3}6$ (40)

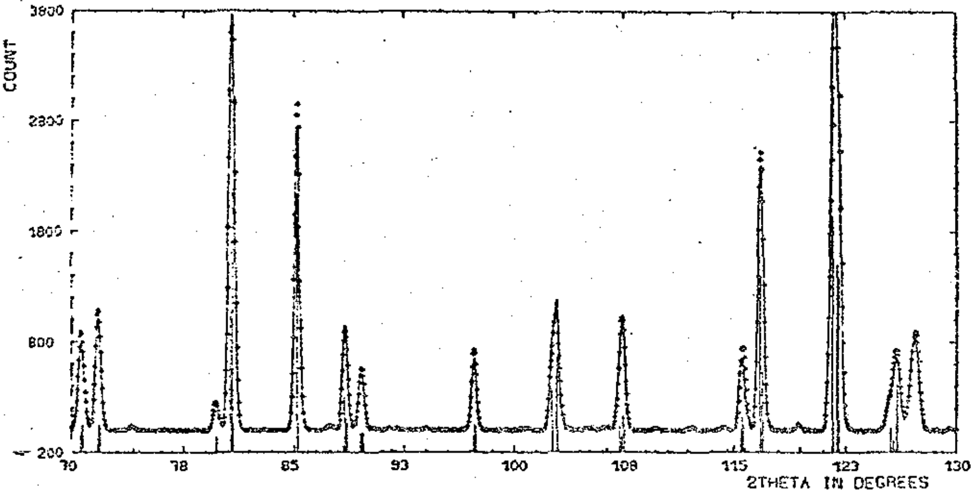
	125K (Fm3m)	107K (C4/mmc)	90K (C2/c)	30K ($P2_1/n$)	5K ($P2_1/n$)
B(Cℓ3)	2.07	2.23 (16)	1.33 (30)	0.89 (6)	0.48 (5)
	2.07	2.23	1.95 (35)	0.89	0.48
	0.39	0.10 (11)	0.34 (16)	0.89	0.48
	0.	0.	0.33 (16)	0.	0.
	0.	0.	1.37 (19)	0.	0.
	0.	0.	0.31 (39)	0.	0.
a	9.7754 (1)	9.7602 (1)	9.7329 (2)	6.8884 (1)	6.8877 (1)
b	9.7754	9.7602	9.7835 (2)	6.8713 (1)	6.8673 (1)
c	9.7754	9.7833 (2)	9.7673 (3)	9.7875 (2)	9.7926 (2)
β	90.	90.	90.046 (4)	90.078 (3)	90.090 (3)
	934.11 (2)	932.00 (3)	930.06 (4)	926.52×2 (4)	926.38×2 (2)
R_1	3.8	6.0	6.7	4.9	4.6
X^2	7.7	11.1	10.3	8.8	8.9

Table 3

125K (Fm3m)	107K (C4/mnc)	90K (C2/c)	30K ($P2_1/n$)	5K ($P2_1/n$)
2.346 (1)	2.314 (2)	2.337 (3)	2.353 (4)	2.351 (3)
2.346	2.314	2.338 (4)	2.360 (4)	2.355 (3)
2.346	2.382 (3)	2.375 (5)	2.365 (3)	2.361 (3)
90.	90.	90.6 (2)	90.3 (2)	90.0 (2)
90.	90.	90.8 (2)	90.8 (2)	90.3 (2)
90.	90.	91.4 (3)	91.2 (2)	91.6 (2)

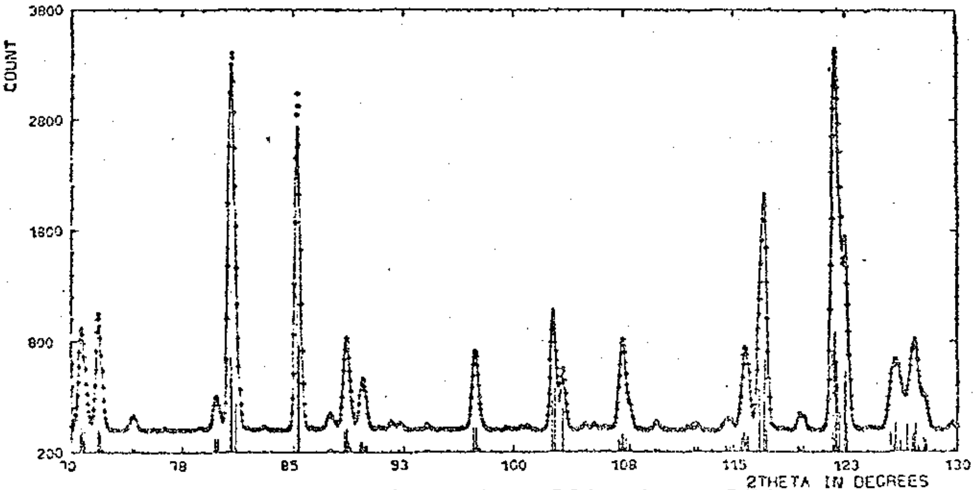


K2RECL6 AT 125K ON D1A AT 1.909A FM3M 16MM V CAN M

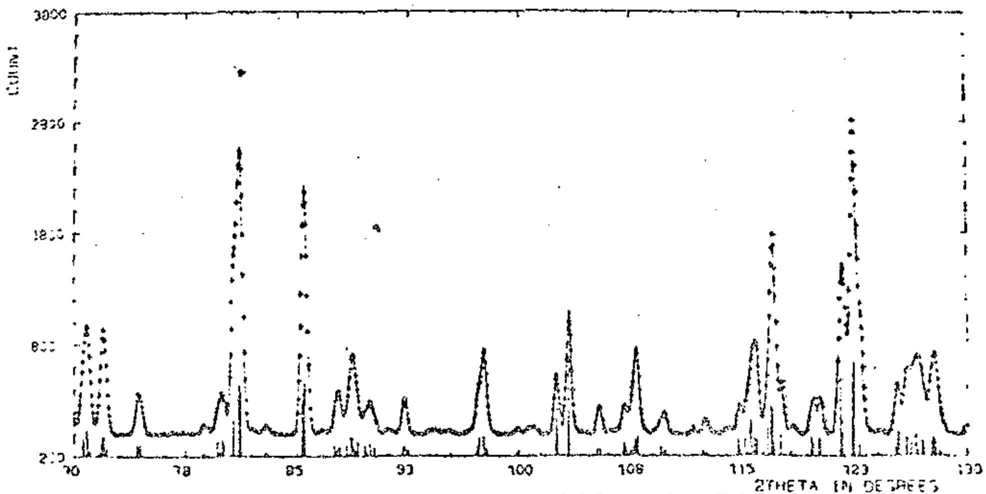


K2RECL6 AT 107K ON D1A AT 1.909A P4/MNC TET 16MM V

Scale wrong. -200!



K2RECL6 AT 90K ON D1A AT 1.909A C2/C DEC'78



K2RECL6 AT 30K ON D1A AT 1.909A MON=50K=37S 16MM V

FIGURE 1

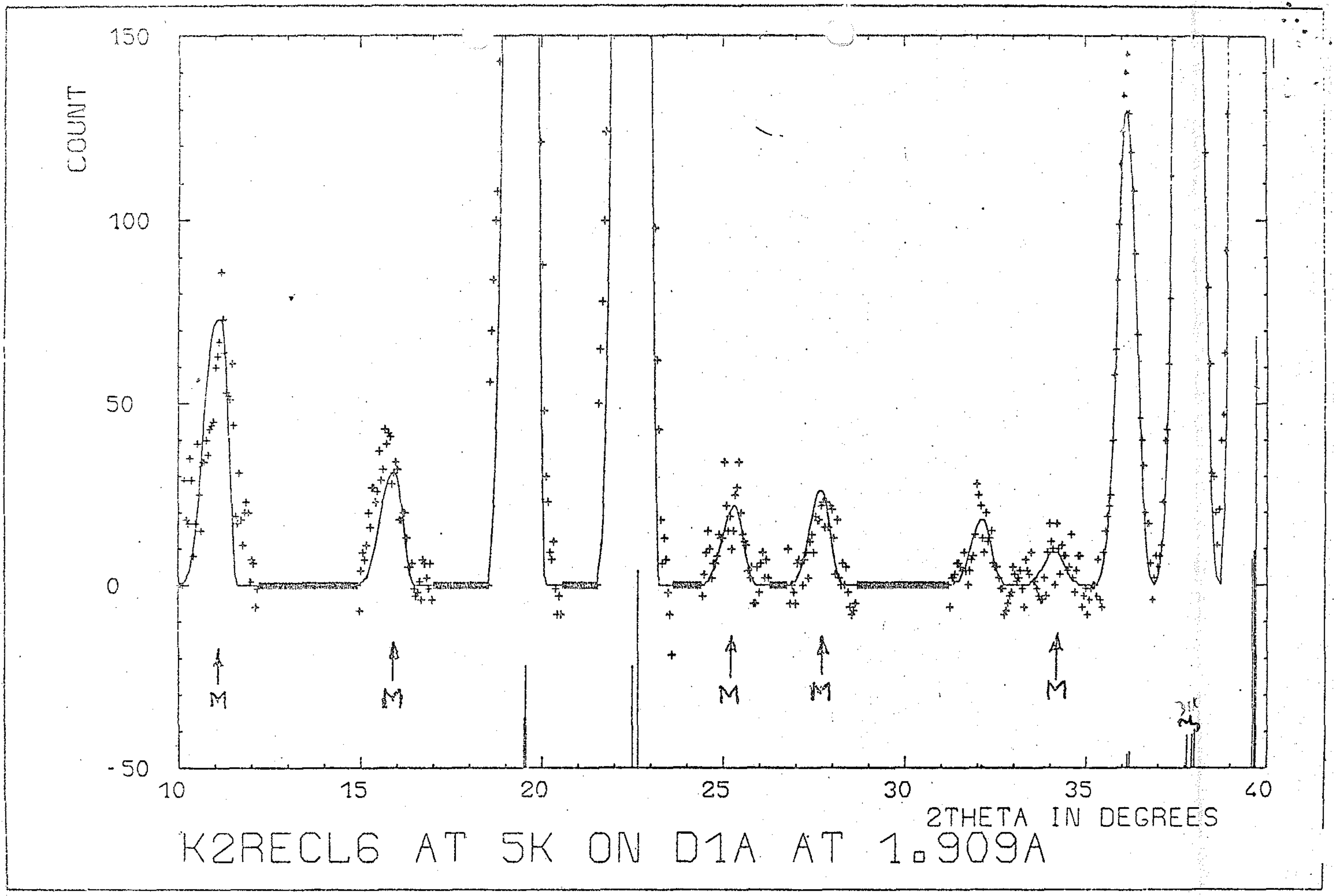

COUNT
150
100
50
0
-50
10
15
20
25
30
35
40
2THETA IN DEGREES
M
M
M
M
M
K2RECL6 AT 5K ON D1A AT 1.909A

FIGURE 2'

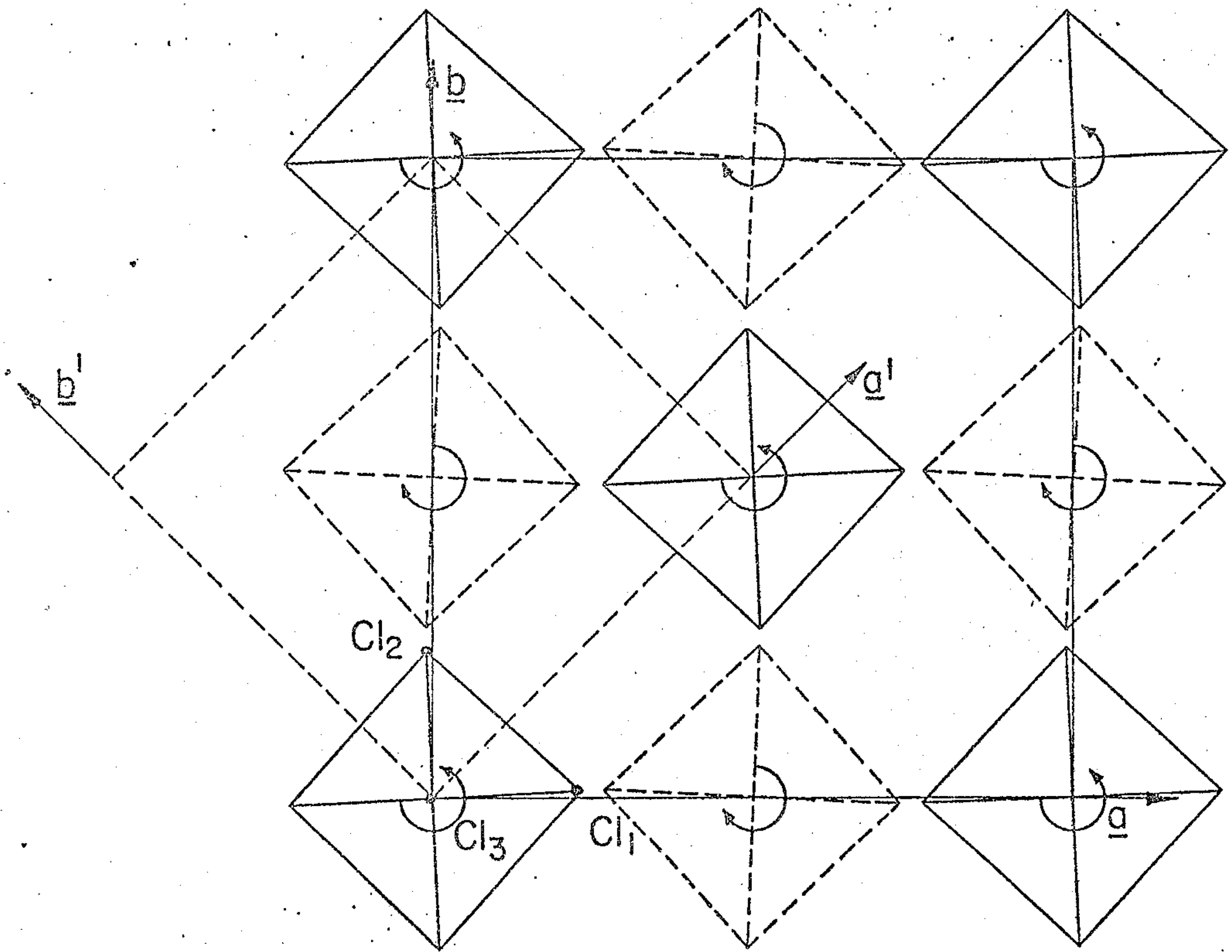


FIGURE 2.

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