# 276. *The Crystal Structure of Ammonium Nitrate III, and Atomic Scattering Factors in Ionic Crystals.*

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The crystal structure of ammonium nitrate III has been redetermined in the light of revised optical and *X*-ray evidence.

In the course of an investigation into the conditions of stability of ammonium nitrate III, the form normally stable from 32·3° to 84·2°, we measured the series of single-crystal rotation and oscillation photographs which we obtained, and compared our data with those of Hendricks, Posnjak, and Kracek (*J. Amer. Chem. Soc.*, 1932, **54**, 2776). Although there is general agreement between their observations and ours, there are certain marked discrepancies [see information in Tables II and III concerning the planes (002) and (004), (101), and (200)]. Moreover, there are frequently wide discrepancies between their observed and calculated intensities, as, for example, for the planes observed to have " moderate " intensities.

We are unable to account for the observational discrepancies, but for the rest, it seems possible that the authors were aware of the optical data which Hendricks, Deming, and Jefferson published later (*Z. Krist.*, 1933, **85**, 145) and, believing them to be correct, proposed a structure in conformation with them. They say that their agreement between observed and calculated intensities is only moderate. A difficulty in trying to explain these discrepancies is that although the authors state that the interfacial angles between the needle zone faces is 90° 0′ (faces therefore *a* {100} and *b* {010}) they quote no data derived directly from rotation, oscillation, or Weissenberg photographs about the *a*- or *b*-axes apart from the intensities of {001} which we consider erroneous and for which they fail to record calculated intensities. We therefore decided to redetermine the structure.

Since ammonium nitrate III is stable only above 32°, all manipulations of the crystals had to be carried out above this temperature. The specimens used were grown from aqueous-alcoholic solution in a thermostatic hot-air chamber at 50°, and selected and mounted while still in the chamber. They were then rapidly transferred to the goniometer arcs while a stream of hot air at *ca.* 42° was allowed to flow over crystal and arcs alike. Optical goniometry revealed that the crystals, which were long needles, usually had only the four prism faces of the {110} form present, the angle (110);($1\bar{1}0$) being 94°. There is probably no significance in this difference of habit between our crystals and those of Hendricks *et al.*

After the camera had been placed in position, hot air was introduced into it by a wide tube inserted through the lid and reaching down to near the level of the crystal, a thermometer being present in the air stream to ensure maintenance of a sufficiently high temperature (*ca.* 42°). The *X*-radiation employed was from the copper target of a Shearer tube with a nickel-foil filter. The following axes were measured : $a = 7{\cdot}14$, $b = 7{\cdot}65$, $c = 5{\cdot}83$ A. These compare satisfactorily with the results of Hendricks *et al.*, *viz.*, $a = 7{\cdot}06$, $b = 7{\cdot}66$, $c = 5{\cdot}80$ A. Examination of oscillation photographs about the *a*, *b*, and *c* axes revealed $\{0kl\}$ present only when $k$ is even, $\{h0l\}$ present only when $h + l$ is even, $\{hk0\}$ and $\{hkl\}$ present in all orders. These extinctions are consistent with the space-group *Pbnm* ($V_h^{16}$) assumed by the American investigators although *Pbn* ($C_{2v}^9$) is also possible. For preliminary calculations the space-group of higher symmetry *Pbnm* was assumed.

The structure factors for planes of the $\{hk0\}$ zone are the same for both space-groups and, as is shown later, the atomic positions were deduced by constructing a Fourier projection on (001). Since it was impossible to carry out work with heated crystals on the Weissenberg instrument available, visual estimates of intensities had to be made from rotation and oscillation photographs, with consequent limitations of accuracy. It was found possible, using the atomic positions definitely located by the Fourier synthesis, to postulate a structure based on the symmetry elements of *Pbnm*, giving satisfactory agreement between observed and calculated intensities within the limits of accuracy of the work. In addition, the packing of the atoms in the unit cell is such that there is little possibility of changes in the relative positions indicated if on the one hand the projection on (001) is to be maintained while on the other the space-group is to be altered to *Pbn*; any such changes would increase the range of $NH_4$ . . . . O distances observed on the structure. Thus we consider that the choice of the space-group of higher symmetry, *Pbnm*, is justified.

In this space-group, then, eight asymmetric units are required, four being mirror images of the others, but as only four $NH_4NO_3$ units, *i.e.*, four $NH_4^+$ and four $NO_3^-$ ions, are present, these must possess two-fold symmetry; since the space-group does not involve axes of rotation, the ions are restricted to central or planar symmetry. Both these types need to be considered for, though neither the tetrahedral $NH_4^+$ nor the planar $NO_3^-$ group can have a centre of inversion when " at rest ", in ammonium nitrate I, the form stable from 125° to the melting point at 169·5°, there is only one ion of each species in a cubic cell and therefore each must be rotating in a way which enables it to simulate cubic symmetry. In ammonium nitrate III rotation of the $NH_4^+$ and $NO_3'$ could confer on them pseudo-central symmetry. On the other hand, (*a*) the latter modification is stable at considerably lower temperatures and its ions are therefore less likely to be rotating in the solid state, and (*b*) the number of ions present is the minimum required if they are planar and at rest. We decided, therefore, to begin by placing the nitrate ions on the symmetry planes, but in view of the fact that the ammonium ions are more nearly spherical and therefore more readily capable of free rotation, we decided to consider their location at centres of inversion and on planes of symmetry in turn. In the latter case the co-ordinates of the ammoniacal nitrogen are :

$$(a)\ u_A, v_A, \tfrac{1}{4};\ \ u_A, \bar{v}_A, \tfrac{3}{4};\ \ \tfrac{1}{2} - u_A, \tfrac{1}{2} + v_A, \tfrac{1}{4};\ \ \tfrac{1}{2} + u_A, \tfrac{1}{2} - v_A, \tfrac{3}{4}.$$

In the former they may be either :

$$(b)\ 0, 0, 0;\ \ 0, 0, \tfrac{1}{2};\ \ \tfrac{1}{2}, \tfrac{1}{2}, 0;\ \ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2},\quad \text{or}\quad (c)\ \tfrac{1}{2}, 0, 0;\ \ \tfrac{1}{2}, 0, \tfrac{1}{2};\ \ 0, \tfrac{1}{2}, 0;\ \ 0, \tfrac{1}{2}, \tfrac{1}{2}.$$

For the nitrate ions two dispositions on the symmetry planes of the crystal are possible, *viz.*, so that all four atoms of each ion are on the (same) symmetry plane or so that the nitrogen and one oxygen are on the plane, the other oxygens being above and below this. In the first case pronounced negative optical birefringence would occur, the minimum refractive index $\alpha$ being perpendicular to the symmetry planes, *i.e.*, parallel to the *c*-axis (cf. potassium nitrate and aragonite; Bragg, " Atomic Structure of Minerals ", Oxford Univ. Press, 1937, pp. 119 *et seq.*). In the second, $\gamma$, the greatest refractive index, would be parallel to *c*. In fact, $\gamma$ is parallel to *c*, so that the second possibility is the correct one; since the optic axial angle is high ($2V \approx 90°$) it follows that the plane of the ion must be quite oblique to both the *a* and the *b* axis.

The atomic co-ordinates of N and one O of the $NO_3^-$ must therefore be as in (*a*) above but with parameters $u_N$, $v_N$ and $u_O$, $v_O$. The other oxygens are in general (*i.e.*, eight-fold) positions :

$$\begin{aligned}(d)\ & x, y, z;\ \ \bar{x}, \bar{y}, \tfrac{1}{2} + z;\ \ \tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z;\ \ \tfrac{1}{2} + x, \tfrac{1}{2} - y, \bar{z};\\ & x, y, \tfrac{1}{2} - z;\ \ \bar{x}, \bar{y}, \bar{z};\ \ \tfrac{1}{2} - x, \tfrac{1}{2} + y, z;\ \ \tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} + z.\end{aligned}$$

To locate the various atoms, we first considered the orders of (001) since they involve only the *z*-co-ordinates. For those the structure factor $F_{00l}$ is :

$$F_{00l} = 8f(O) \cos 2\pi lz + 4f(O) \cos 2\pi \frac{l}{4} + 4f(N) \cos 2\pi \frac{l}{4} + 4f(A) \cos 2\pi \frac{l}{4},$$

or

$$F_{00l} = 8f(O) \cos 2\pi lz + 4f(O) \cos 2\pi \frac{l}{4} + 4f(N) \cos 2\pi \frac{l}{4} + 4f(A) \cos 2\pi \frac{l}{2}$$

according as the ammonium ion is situated on the symmetry plane or at a symmetry centre; f(O), f(N) and f(A) are the atomic scattering factors of oxygen, nitrate nitrogen, and ammonium respectively. Hendricks, Posnjak, and Kracek " assumed that f(A) for Cu-*K* radiation is approximately the same as determined for Mo-*K* radiation diffracted from $NH_4Cl$ (Wyckoff and Armstrong, *Z. Krist.*, 1929, **72**, 319), that f(O) is the same as for oxygen in nickel oxide (Cu-*K* radiation) (Wyckoff, *Physical Rev.*, 1930, **35**, 583; " Structure of Crystals ", 2nd Edn., 1931, p. 100), and that f(N) = 0·35 f(O) independent of $\sin \theta/\lambda$ ". It is thus implied that, so far as the diffraction of *X*-rays is concerned, the nitrate ion approximates to a $N^{5+}$ ion surrounded by three $O^{2-}$ ions. In view of the completed *L* shells of nitrogen and oxygen in nitrate ions as formulated by chemists, we have preferred to regard the f values of these atoms as the same, with $f_0(N) = f_0(O) = 8$, $f_0$ being the value of f when $\theta = 0$. Of the various theoretical arguments in support of this view, we quote only two. It is well known that the polarising power of a cation increases with increasing charge and decreasing radius. Since the " radii " of $N^{5+}$ and, say, $Li^+$ are quoted by, *e.g.*, Pauling (" Nature of the Chemical Bond ", 2nd Edn., p. 346) as 0·11 and 0·60 A., respectively, it follows that the polarising power of the $N^{5+}$ will be so great as to lead to N–O bonds which are essentially covalent. Secondly, the uniformity of structure of the nitrate ion as a planar equilateral triangle in which the central nitrogen has no tendency to be surrounded by more than three oxygens or other " anions ", shows that the N–O bonds are directed in space and therefore are covalent, not electrovalent.

Using, then, these atomic scattering factors, we found that if the $NH_4^+$ ion is on the mirror plane $z$ must have a value of between 0·06 and 0·07 in order to account for the observed relative intensities of (002), (004) and (006); $z$ was selected as 0·06, equivalent to a distance of about 2·21 A. for O . . . . O in the nitrate ion, or 1·27 A. for N . . . .O, which latter value lies between the measurement of 1·21 A. made by Elliott (*J. Amer. Chem. Soc.*, 1937, **59**, 1380) for the nitrate ion in sodium nitrate, and the value of 1·31 A. calculated by Pauling on the basis of one double bond resonating between the three positions. If the ammonium ion was placed at a symmetry centre no such satisfactory relative intensities could be calculated.

We next drew, on scaled diagrams of the (001) plane, the traces of various particularly strong and particularly weak $\{hk0\}$ planes (excluding space-group halvings). On examining the resulting diagram with the assistance of a scale model of the nitrate ion (edge = O . . . . O proportional to 2·21 A.), arranged so that one O . . . . O direction was perpendicular to the diagram, tentative positions for the atoms of this ion were obtained which permitted a reasonable location of the $NH_4^+$ ion on the symmetry plane. From these we calculated, after some slight adjustments, structure factors which were in approximate agreement with our qualitative estimates of intensity. In an endeavour to refine the structure we then made by visual estimation numerical assays of the intensities of as many as possible of the $\{hk0\}$ planes from rotation and oscillation photographs and constructed a Fourier projection on (001).

This projection proved far from satisfactory because, while indicating unequivocally the two oxygens in the general positions (*d*), it left considerable doubt as to the placing of the ammonium ion and the third oxygen on the reflection planes. One of these was revealed as a definite peak in the landscape but the other only as an upland region. According to whether and where the ammonium or oxygen is placed in this upland region three alternative structures are obtained which give F values for the $\{hk0\}$ planes of roughly the same magnitude as those estimated visually. However, by trial and error methods the ammonium ion was eventually placed in this region in a position which led to satisfactory agreement with the intensities of reflections over all three principal zones as well as for the $\{hkl\}$ planes. The nitrate nitrogen was suitably located on the line joining the " special " and " general " oxygens in the projection. In view of the large changes in structure amplitude brought about in certain planes by movements of the atoms of less than one-hundredth of the cell edge, and the impossibility of testing all the combinations of atomic positions within the tolerances allowed by the Fourier synthesis, the agreement between observed and calculated intensities is as good as can be expected.

TABLE I.

*Atomic co-ordinates.*

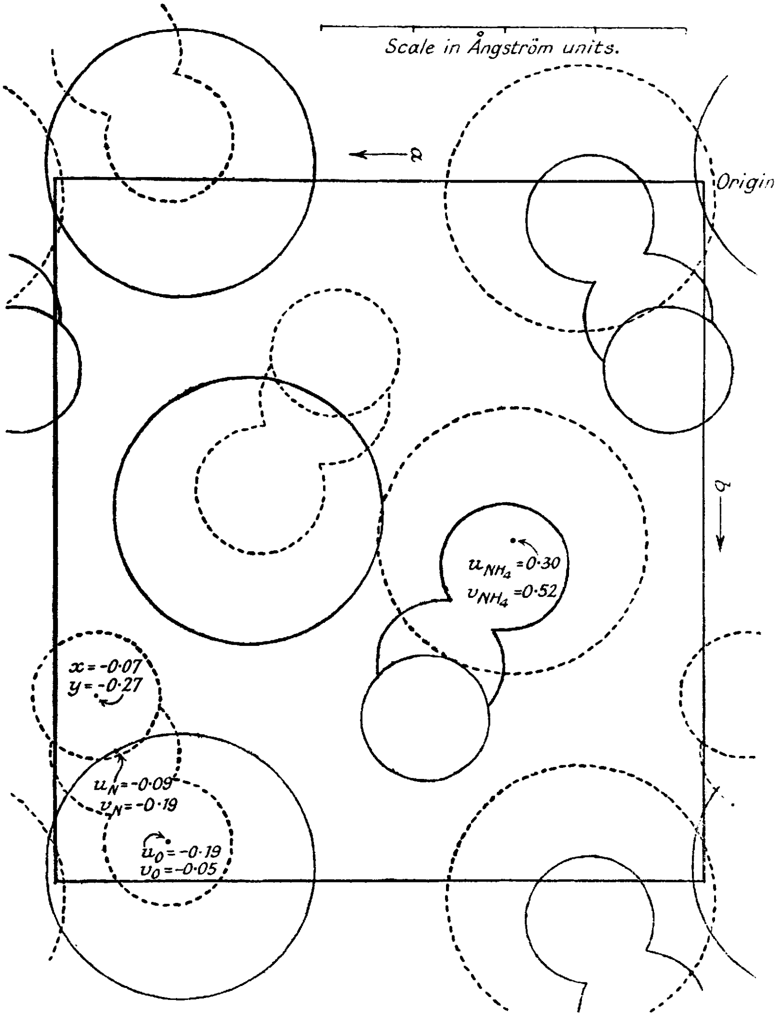
| | | |
|---|---|---|
| $x$ = 0·05—*0·06* | $y$ = 0·17—*0·175*—0·18 | $z$ = *0·06*—0·07 |
| $u_N$ = 0·13—*0·14* | $v_N$ = 0·14—*0·145*—0·15 | $w_N$ = *0·25* |
| $u_O$ = *0·30*—0·29 | $v_O$ = 0·08—*0·085*—0·09 | $w_O$ = *0·25* |
| $u_{NH_4}$ = 0·30—*0·32* | $v_{NH_4}$ = −*0·02* to −0·03 | $w_{NH_4}$ = −*0·25* |

Table I gives the limits within which we consider the parameters of the various atoms to lie, the figures in italics being those used in calculating the structure factors and intensities of Tables II, III, and IV.

Since the crystals were thin needles of nearly square cross-section, it was considered unnecessary to apply absorption corrections to the observed intensities of the $\{hk0\}$ planes. They have, however, been applied to those of the other prism zones, though not to the $\{hkl\}$ planes, calculations of which were made rather as a final check.

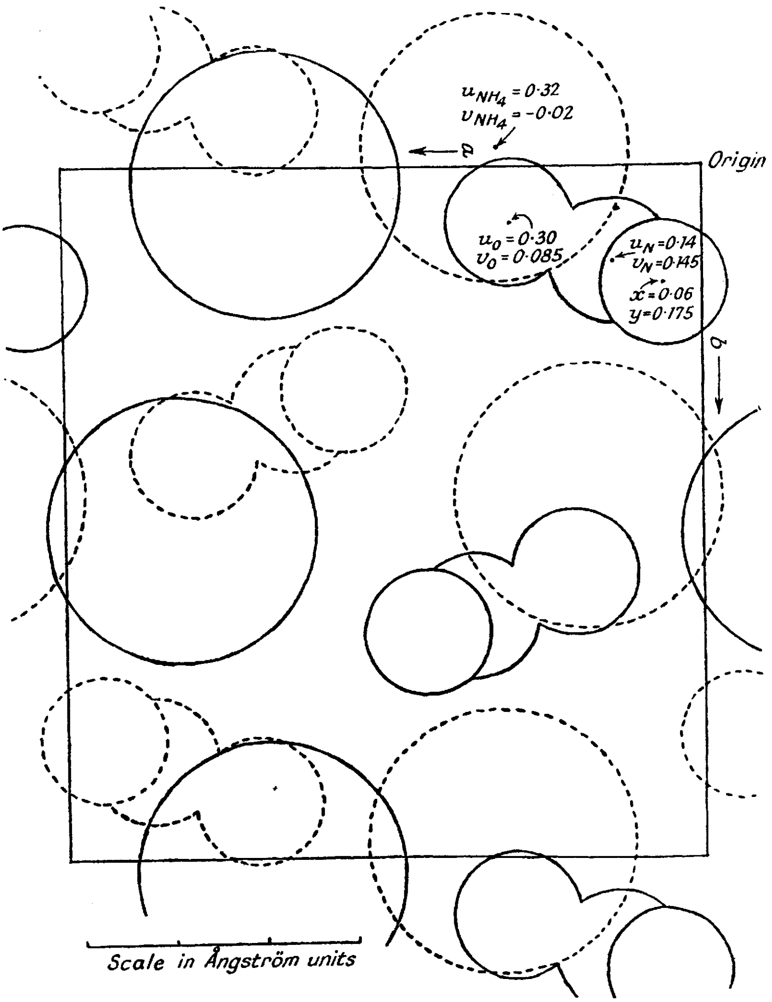
In Table II are given first the observed intensities of the planes of the $\{hk0\}$ zone. Then in col. 3 are recorded the structure factors calculated from the final ionic model, the four atoms of the nitrate ion all being supposed to have the same atomic scattering factors with $f_0(O) = f_0(N) = 8$. Col. 4 gives the factor $L = (1 + \cos^2 2\theta) \sin 2\theta$ by which $F^2$ is converted into the intensity $I$, recorded in col. 5. Cols. 6 and 7 record the intensities observed and calculated by Hendricks *et al.* Table III contains the absorption corrections where applied; these were calculated from the lengths of the paths of the $X$-ray beam through the crystals and the mass absorption coefficients recorded in the " International Tables for the Determination of Crystal Structures," 1933, Vol. II, p. 577. Apart from this, Tables III and IV will be readily understood by comparison with Table II.

FIG. 1.



It will be seen that our observed and calculated results are in better agreement than those of Hendricks, Posnjak, and Kracek. The principle difference between the two structures is in the disposition of the nitrate ions, which in our model (Fig. 1) are more nearly parallel to the *a*- than to the *b*-axis, the converse being the case with the structure reported by the Americans (Fig. 2). Our proposal would therefore lead to refractive indices $\alpha//b$, $\beta//a$, $\gamma//c$ The measured values as recorded by Hendricks, Deming, and Jefferson (*Z. Krist.*, 1933, **85**, 145) are $\alpha = 1{\cdot}463/a$, $\beta = 1{\cdot}543//b$, and $\gamma = 1{\cdot}600//c$. Our own measurements, carried out on mounted crystals of known orientation (as determined by *X*-rays) agree with these numerically, but we find *a*//*b* and $\beta//a$. In view of the fact that the crystals are long needles with their needle zone faces at or nearly at right angles, it is not surprising that the vibration directions of the fast and medium rays should have been wrongly identified. Thus the revised optical properties support our proposed ionic arrangement. In our structure the $NH_4^+$ ions are distant 2·7—3·2 A. from their nearest oxygen neighbours, while in theirs the mean of nine such distances ranging from 2·75 to 3·13 A. is 2·95 A.

FIG 2.



FIGS. 1 and 2.—*Fig.* 1 *represents the unit cell of ammonium nitrate III deduced in this investigation, projected parallel to the* c*-axis ; Fig.* 2 *is a similar projection of the structure of Hendricks, Posnjak, and Kracek. The unbroken and the dotted circles represent atoms located on or about reflection planes at* $c = \frac{1}{4}$ *and* $\frac{3}{4}$, *respectively. The large circles represent ammonium ions (Pauling's radius* 1·48 A.), *while the groups of small circles represent the nitrate ions, and oxygens in the general positions being superimposed one on another in the projection. The radii of oxygen and nitrogen are taken as Pauling's covalent radii* (0·66 A. *and* 0·70 A., *respectively*).

TABLE II.

| *hk*0. | Intensity, obs. num. | F, calc. | *L.* | Intensity: | | |
|---|---|---|---|---|---|---|
| | | | | G. & W., calc. | H., P., & K., obs. | calc. |
| 200 | 500 | −10 | 4·5 | 450 | vw | 8 |
| 400 | 130 | −12 | 1·7 | 250 | vw | 8 |
| 600 | — | −10 | 1 | 100 | vw | — |
| 020 | 0—30 | 7 | 4 | 200 | vw | 1 |
| 040 | 1300 | −14 | 2 | 400 | m | 660 |
| 060 | 800 | 30 | 1 | 900 | w | — |
| 110 | 1000 | 15 | 6·5 | 1450 | m | 550 |
| 210 | 8000 | −44 | 3·75 | 7000 | vvs | 3000 |
| 310 | 2600 | 38 | 2·5 | 3600 | mms | 10 |
| 410 | 1800 | −35 | 1·7 | 1750 | s | 400 |
| 510 | 800 | −31 | 1·25 | 1200 | m | — |
| 610 | — | − 3 | 1 | 10 | — | — |
| 120 | 5000 | −45 | 4 | 8000 | ms | 370 |
| 220 | 10,000 | −44 | 3 | 6000 | s | 500 |
| 320 | 1300 | −28 | 2 | 1600 | m | 90 |
| 420 | 260 | 1 | 1·5 | — | w | 50 |
| 520 | 400 | −15 | 1·25 | 250 | w | — |
| 130 | 10,000 | −60 | 2·75 | 9900 | s | 270 |
| 230 | 500 | 4 | 2·2 | 40 | mw | 140 |
| 330 | 500 | 20 | 1·7 | 700 | vw | 80 |
| 430 | 130 | — | 1·35 | — | w | — |
| 530 | — | 3 | — | 10 | — | — |
| 140 | 250 | 14 | 1·8 | 350 | a | 200 |
| 240 | 130 | 10 | 1·7 | 170 | a | 15 |
| 340 | 2300 | 31 | 1·4 | 1300 | mms | — |
| 440 | 130 | 4 | 1·1 | 20 | — | — |
| 540 | — | 8 | 1 | 64 | — | — |
| 150 | 800 | 15 | 1·5 | 350 | — | — |
| 250 | 260 | 21 | 1·3 | 500 | — | — |
| 350 | 500 | 14 | 1·2 | 270 | — | — |
| 450 | — | − 3 | 1 | 10 | — | — |
| 160 | — | 15 | — | — | — | — |
| 260 | — | 10 | — | — | — | — |
| 360 | — | − 5 | — | — | — | — |

TABLE III.

| *h*0*l* or 0*k* . | Intensity, obs. | F, calc. | Abs., corr. | *L.* | Intensity, calc. | |
|---|---|---|---|---|---|---|
| | | | | | G. & W. | H., P., & K. |
| 101 | ms | 22 | 2 | 5 | 1125 | 4000 |
| 103 | vw—a | 4 | 1·8 | 1·8 | 16 | — |
| 105 | w | 11 | 2·2 | 1·0 | 50 | — |
| 202 | s | 58 | 2·3 | 2·45 | 4000 | 750 |
| 204 | m | 24 | 2·3 | 1·2 | 310 | — |
| 206 | w | 8 | ? | 1·2 | ? | — |
| 301 | vw | 14 | 12·5 | 2·4 | 40 | 200 |
| 303 | mw | 21 | 3·3 | 1·5 | 200 | 160 |
| 305 | vw | 16 | ? | 1·0 | ? | — |
| 402 | a | 10 | 10 | 1·4 | 14 | 3 |
| 404 | a | 8 | ? | 1 | ? | — |
| 406 | a | 7 | 10 | 1·2 | 5 | — |
| 501 | w | 8 | 3 | 1·2 | 25 | — |
| 503 | vw | 20 | ? | 1 | ? | — |
| 505 | vw | 6 | ? | 1·5 | ? | — |
| 002 | s | 37 | — | 3·4 | 4630 | — |
| 004 | m | 31 | — | 1·3 | 1250 | — |
| 006 | w | 23 | — | 1·1 | 580 | — |
| 021 | s | 54 | 3·3 | 3·7 | 4000 | 70 |
| 023 | vw | 11 | 2·1 | 1·7 | 90 | — |
| 025 | mw | 32 | ? | 1 | ? | — |
| 022 | s | 54 | 2·1 | 2·5 | 3450 | 1250 |
| 024 | mw | 23 | 2·1 | 1·2 | 300 | — |
| 026 | a | 9 | ? | 1·1 | ? | — |
| 041 | a | 6 | 4·5 | 1·8 | 15 | 20 |
| 043 | mw | 35 | 4 | 1·25 | 375 | 10 |
| 045 | a | 4 | ? | 1·1 | ? | — |
| 042 | a | 8 | 4 | 1·4 | 20 | 2 |
| 044 | a | 1 | 4 | 1 | 0 | — |
| 046 | a | 3 | ? | 1·7 | ? | — |

TABLE IV.

| | | | *I*, calc. | | | | | | *I*, calc. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *hkl.* | *I*, obs. | F, calc. | *L.* | G. & W. | H., P., & K. | *hkl.* | *I*, obs. | F, calc. | *L.* | G. & W. | H. P., & K. |
| 111 | s | 23 | 4·7 | 2500 | 1300 | 151 | w | 22 | — | — | — |
| 211 | s | 32 | 3·5 | 3500 | 15 | 251 | w | 20 | 1·2 | 480 | — |
| 311 | vw | 3·5 | 2 | 20 | 0 | 112 | s | 23 | 2·9 | 1550 | 400 |
| 411 | w | 8 | 1·5 | 100 | 7 | 212 | vw | 5 | 2·4 | 60 | 80 |
| 511 | w | 13 | 1·2 | 200 | — | 312 | mw | 20 | 1·7 | 680 | 280 |
| 121 | ms | 25 | 3·5 | 2200 | 240 | 412 | mw | 17 | 1·3 | 380 | 140 |
| 221 | w | 8 | 2·6 | 170 | 30 | 122 | m | 16 | 2·4 | 700 | 280 |
| 321 | mw | 7 | 1·9 | 100 | 130 | 222 | mw | 11 | 2 | 250 | 65 |
| 421 | a | 9 | 1·4 | 110 | 2 | 322 | mw | 16 | 1·5 | 380 | 15 |
| 521 | vw | 8 | 1·1 | 70 | — | 422 | w | 3 | 1·4 | 13 | 3 |
| 131 | mw | 8 | 2·4 | 150 | 100 | 132 | a | 3 | 1·8 | 16 | 10 |
| 231 | w | 5 | 2 | 50 | 5 | 232 | w | 7 | 1·6 | 80 | 100 |
| 331 | vw | 10 | 1·6 | 160 | 37 | 332 | ms | 34 | 1·4 | 1500 | 0 |
| 431 | mw | 23 | 1·3 | 650 | — | 432 | vw | 6 | 1·1 | 40 | — |
| 141 | m—ms | 40 | 1·7 | 2700 | 4 | | | | | | |
| 241 | m | 23 | 1·5 | 750 | 70 | | | | | | |
| 341 | a | 5 | 1·35 | 30 | — | | | | | | |
| 441 | w | 6 | 1·1 | 40 | — | | | | | | |

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