use of (5) did not lead to errors greater than 3% for small angles of missetting.

The values of d^* as calculated from (5) gave, in turn, interplanar spacings of 542, 390 and 330 A. for directions perpendicular to (110), (100) and (111) respectively. These spacings are in the ratios $1/\sqrt{2} : 1 : 2/\sqrt{3}$, indicating a cubic body-centred lattice with a cell side of 386 A.

In general, the procedure outlined above gives directly the interplanar spacings of planes of reciprocal points perpendicular to any chosen crystallographic axes set parallel to the X-ray beam. Bravais lattices and cell dimensions are accordingly not difficult to determine for crystals of large unit cells, especially if the crystals are well formed.

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The Crystal Structure of Sodium Selenochromite, NaCrSe₂, and Preliminary Investigations on Related Compounds

By W. Rüdorff
Chemisches Institut der Universität, Tübingen, Germany
W. R. Ruston
Association pour les Études Texturales, 4 rue Montoyer, Brussels, Belgium
and A. Scherhaufer
Institut für anorganische und analytische Chemie, Technische Hochschule, Vienna, Austria

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Attempts have been made to prepare new model-substances for magneto-chemical investigations. Sodium selenochromite, $NaCrSe_2$, rubidium selenochromite, $RbCrSe_2$, and rubidium thiochromite, $RbCrS_2$, of high purity have been prepared by reaction of the pure elements, and a potassium selenochromite, $K_{0\cdot5}CrSe_2$ or $KCrSe_2 . CrSe_2$, by fusion of KCN with Cr_2O_3 and selenium.

The crystal structures of the alkali selenochromites and rubidium thiochromite have been investigated with the following results:

$NaCrSe_2$: hexagonal rhombohedric; D^5_{3d}–$R\bar{3}m$; $I_a = 3\cdot708$ A., $I_c = 20\cdot29$ A. $\pm 0\cdot05$ A.; parameter z of Se: $95\cdot3° \pm 0\cdot3°$; density obs. $= 4\cdot49_7$ g.cm.$^{-3}$; density calc. $= 4\cdot77$ g.cm.$^{-3}$; the hexagonal unit cell contains three, the rhombohedral cell one molecule of $NaCrSe_2$.

$K_{0\cdot5}CrSe_2$: hexagonal rhombohedric; C^5_{3v}–$R3m$; $I_a = 3\cdot44$ A., $I_c = 24\cdot2$ A.; parameter z of Se: $141\cdot5°$; parameter z of K: 60–62°.

$RbCrSe_2$: hexagonal rhombohedric; space group not yet determined; $I_a = 3\cdot34$ A., $I_c = 26\cdot9$ A.; density obs. $= 5\cdot02$ g.cm.$^{-3}$, density calc. $= 5\cdot26$ g.cm.$^{-3}$

$RbCrS_2$: hexagonal rhombohedric; space group not yet determined; $I_a = 3\cdot39$ A., $I_c = 16\cdot20$ A.

The radius of the Se^{2-} ions decreases from 1·85 A. in $NaCrSe_2$ to $1\cdot71_5$ A. in $RbCrSe_2$. Preliminary magnetic measurements on $NaCrSe_2$ show the compound to obey the Curie-Weiss law with a θ value of about $+70°$ C.

Introduction

The compounds of the transition-group elements with the non-metals of the sixth group differ considerably in their magnetic behaviour from the pure ionic compounds, i.e. the salts and the oxygen-containing acids. Commonly they show only moderate paramagnetism or ferromagnetism. To explain this behaviour Haraldsen & Klemm (1934) assumed that covalent bonds are developed between the cations. To correlate the formation of such covalent bonds with the distances between the cations in the crystal structure it seemed useful to investigate model substances, in which for structural reasons the development of covalent bonds occurs in one direction only.

Rüdorff & Stegemann (1943) realized this condition in the alkali thiochromites. These compounds have the

$NaHF_2$ structure consisting of hexagonal chromium-, alkali metal- and sulphur-layers, the chromium-layers being separated from each other by two sulphur- and one alkali metal-layer. Covalent bonds between the chromium ions can occur in this arrangement only along the layers, because the distance of the chromium ions from layer to layer across the sulphur- and alkali metal-layers is too great. Since the spacing between chromium ions within the layers depends on the dimensions of the alkali metal ions and of the anions, it can be changed and its influence on the formation of covalent bonds can be investigated by isomorphous substitution.

Rüdorff & Stegemann examined the effect of the chromium spacing by means of magnetic measurements, using sodium thiochromite, $NaCrS_2$, of which the structure was first determined by Boon & MacGillavry (1942), and potassium thiochromite, $KCrS_2$. Their main results are given in Table 1, in which θ is the Curie temperature. The experiments reported in this paper have been carried out in order to find other suitable model substances fulfilling the structural conditions mentioned above, and to develop methods for their preparation in a state of high purity, as required for magnetic measurements.

Table 1. Cr–Cr *spacings and Curie temperature of* Cr_2S_3 *and the alkali thiochromites*

Compound	Cr–Cr spacing in A.	θ °C.	Interaction between the Cr ions
Cr_2S_3	2·78 and 3·42	—	Very strong covalent bonds with antiparallel spin
$NaCrS_2$	3·53	+ 37	Weak covalent bonds with parallel spin
$KCrS_2$	3·62	+116	Strong covalent bonds with parallel spin

Preparation of the alkali selenochromites

While in the series of the thiochromites several other salts are known besides the alkali compounds, only the potassium salt has hitherto been prepared among the corresponding selenochromites. Milbauer (1903) obtained this compound by fusion of KCN with Cr_2O_3 and Se.

In a preliminary experiment an attempt was made to prepare sodium selenochromite by Milbauer's method, substituting KCN by NaCN. The result, however, was found to be unsatisfactory; the X-ray powder photographs of the samples indicated a partial decomposition following the extensive digestion with dilute NaOH, to which the fusion had to be subjected to separate the crystals. Another method which permitted the preparation of the compounds from the pure elements was therefore adopted. Chromium selenide, Cr_2Se_3, and the alkali selenides were prepared in high purity, the former by the method of Haraldsen & Mehmed (1938), by heating a stoichiometric mixture of powdered electrolytic chromium with pure selenium in an evacuated and sealed quartz phial at 800° C.; the latter by the method of Klemm, Sodomann & Langmesser (1939), by letting the distilled alkali metals react with pure selenium, both elements being dissolved in dry liquid ammonia. Both selenides were then brought to reaction with an excess of pure selenium in an evacuated and sealed quartz phial at 800–1000° C. The excess of alkali polyselenides was extracted with dry liquid ammonia in a specially designed vessel, and the liberated crystals were then very quickly washed with a dilute solution of the corresponding alkali hydroxide and finally with dry alcohol. The selenochromites of sodium and rubidium were thus prepared for the first time; hitherto only the potassium compound had been prepared by Milbauer's method.

The three selenochromites form blue-black to black crystals of high metallic lustre and show under the microscope a well-developed hexagonal shape. Exposed to the humid air they decompose slowly, presumably following the reaction:

$$2\,AlkCrSe_2 + H_2O + CO_2 \rightarrow Alk_2CO_3 + \underbrace{2HCrSe_2 + \tfrac{1}{2}O_2}_{H_2O + \text{chromium selenid}}$$

With non-oxidizing acids chromium selenides are formed, while concentrated HNO_3 or nitro-hydrochloric acid brings about complete solution.

The crystal structure of the alkali selenochromites

Sodium selenochromite, $NaCrSe_2$

The samples used for the determination of the crystal structure gave the following analytical results:

	Obs. %		
	No. 6	No. 9	Calc. %
Na	9·89	9·93	9·87
Cr	22·81	22·26	22·34
Se	67·25	67·75	67·79
Insol. res.	0·04	0·06	—

X-ray powder photographs were made in a camera of 57·2 mm. diameter and single-crystal rotation photographs in a camera of 114·4 mm. diameter, using Ni-filtered Cu $K\alpha$ radiation (wave-length 1·539 A.).

The powder photographs of $NaCrSe_2$ are very similar to those of $NaCrS_2$, and all diffraction lines could be indexed with good agreement to the quadratic form of the hexagonal system (cf. Table 2).

The unit-cell dimensions were determined after correcting for the line shift due to absorption by calibrating with NaCl. The identity period along the a axis was found from the reflexion 11*0 to be

$$I_a = 3{\cdot}708\ \text{A.} \pm 0{\cdot}006\ \text{A.}$$

The correctness of indexing the line (11*0) was proved by a single-crystal rotation photograph, which gave $I_a = 3{\cdot}7$ A. The identity period along the c axis was found from the reflexions 00*9 and 00*12 as

$$I_c = 20{\cdot}29\ \text{A.} \pm 0{\cdot}05\ \text{A.}$$

The calculated density is $d_x = 4{\cdot}77$ g.cm.$^{-3}$ and the density determined with a high-vacuum pycnometer under xylol is $d_f = 4{\cdot}49_7$ g.cm.$^{-3}$ Hence the hexagonal unit cell contains 3 molecules $NaCrSe_2$.

The corresponding rhombohedral cell has

$$I_{\text{rh.}} = 7{\cdot}09_4 \text{ A.}, \quad \alpha = 30{\cdot}3^\circ,$$

and the cell contains 1 molecule $NaCrSe_2$.

The observed reflexions fulfil the rhombohedral condition $h-k+l=3n$. Of the seven rhombohedral space groups, C_{3v}^6–$R3c$ and D_{3d}^6–$R\bar{3}c$ are excluded because there are no threefold positions, and the special extinctions are not in agreement with the observed interferences. In C_3^4–$R3$ and C_{3v}^5–$R3m$ the number of variable parameters makes the determination impracticable. The space groups C_{3i}^2–$R\bar{3}$, D_3^7–$R32$ and D_{3d}^5–$R\bar{3}m$ lead to identical structures, if the existing three- and sixfold positions alone are considered.

D_{3d}^5–$R\bar{3}m$ has the highest symmetry of the five space groups mentioned above, with the following homologous points:

	Hexagonal description:	Rhombohedral description:
Cr:	$0, 0, 0;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}$	$0, 0, 0$
Na:	$0, 0, \tfrac{1}{2};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{5}{6};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{6}$	$\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}$
Se:	$0, 0, z;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3}+z;\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}+z$	x, x, x
	$0, 0, \bar{z};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3}-z;\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}-z$	$\bar{x}, \bar{x}, \bar{x}$

The parameter z of the selenium ions had to be determined by comparison of the observed and calculated intensities. The intensities have been calculated using the atomic scattering factors of James & Brindley (*Internationale Tabellen...*) for the Na^+ ion; for Cr^{3+} the values used for the calculation of $NaCrS_2$ were employed (Rüdorff & Stegemann, 1943); and for Se^{2-} the value for Se was changed in the ratio $F_S : F_{S^{2-}}$. The following observed intensity relations were used in order to determine the parameter z:

$$00{*}6 < 00{*}9, \quad 00{*}9 < 00{*}12, \quad 11{*}6 < 11{*}3,$$
$$11{*}6 < 11{*}9, \quad 10{*}7 < 10{*}11, \quad 11{*}9 < 20{*}10 + 11{*}12.$$

The best agreement with the calculated intensities was obtained with $z = 95{\cdot}3^\circ \pm 0{\cdot}3^\circ$ (cf. Fig. 1), and in Table 2 the estimated intensities are compared with the calculated values. It has to be borne in mind that relative to the $hk{*}l$ reflexions all $00{*}l$ reflexions have an increased intensity on the film, due to orientation of the thin plate-like crystals, while $hk{*}l$ reflexions are weakened.

For a parameter $z = 95{\cdot}3^\circ$, the inter-ionic spacings are the following:

Na–Se: 2·92 A. (2·89 A.); Cr–Se: 2·55 A. (2·55 A.), Se–Se, Na–Na, Cr–Cr within the layers: 3·70 A. (Se^{2-}–Se^{2-}: 3·82 A.).

The values in parentheses are calculated from the Goldschmidt ionic radii.

Fig. 2 shows the rhombohedral unit cell and a scale drawing of the structure of sodium selenochromite.

Preliminary magnetic measurements have shown that sodium selenochromite obeys the Curie-Weiss law with a θ value of about +70° C.

Table 2. *Observed and calculated values of* sin ϑ *and of the intensities for* $NaCrSe_2$

$hk{*}l$	$(\sin\vartheta)_{\text{obs.}}$	$(\sin\vartheta)_{\text{calc.}}$	$I_{\text{estimated}}$	$I_{\text{calc.}} \times 10^{-3}$ for $z = 95{\cdot}3^\circ$
00*3	0·115	0·114	8	54·7
00*6	0·229	0·228	3	18·2
10*1	—	0·243	0	2·3
10*2	0·251	0·251	2	173·0
10*4	0·283	0·283	10	1146·0
10*5	0·305	0·305	1	38·6
00*9	0·341	0·341	4	22·1
10*7	0·357	0·357	6	230·4
10*8	0·386	0·386	9	405·0
11*0	0·415	0·415	7–8	652·0
11*3	0·430	0·430	2	55·0
10*10	0·449	0·448	0·5–1	3·5
00*12	0·455	0·455	5	35·2
11*6	0·473	0·473	1	30·4
20*8	—	0·479	0	0·8
10*11	0·480	0·480	7–8	237·5
20*2	—	0·484	0	55·3
20*4	0·502	0·502	6–7	418·5
20*5	0·513	0·515	0·5	14·6
11*9	0·536	0·537	3	59·0
20*7	0·546	0·547	6	112·4
10*13		0·548		104·0
20*8	0·567	0·567	8	255·8
00*15		0·568		38·5
10*14	—	0·582	0	7·1
20*10	0·613	0·610	5	2·8
11*12		0·615		124·8
20*11	0·633	0·634	4	158·8
12*1		0·635		0·9
12*2		0·637		40·4
12*4	0·650	0·650	7–8	293·0
10*16		0·652		45·6
12*5	—	0·661	0	10·2
00*18	—	0·683	0	7·4
10*17	0·686	0·685	7	96·4
12*7		0·686		95·6
20*13		0·687		81·3
12*8	0·700	0·702	10	208·0
11*15		0·704		195·8
20*14	0·715	0·715	5	4·8

Potassium selenochromite, $KCrSe_2$

We have not yet succeeded in preparing a sample of the composition $KCrSe_2$. The ratio Cr : Se of the samples prepared by the method of Milbauer (1903) was always found to be 1 : 2, but the potassium content was too low and changed from sample to sample. This is probably due to unavoidable hydrolysis during the washing period, when hydrogen, replacing potassium, is readily oxidized:

$$KCrSe_2 + xHOH + \tfrac{1}{2}xO = K_{1-x}CrSe_2 + xKOH + \tfrac{1}{2}xH_2O.$$

Moreover, the samples contained water, which was fairly strongly bound, the composition of samples dried over P_2O_5 in vacuo being approximately $K_{0\cdot5}CrSe_2 . 0{\cdot}5\ H_2O$. Only by heating above 100° C. in vacuo could the water be driven off.

The X-ray powder photographs of the potassium selenochromite compounds permit hexagonal rhombohedral indexing like the other thio- and seleno-compounds. The *a* and *c* axes, however, change in a continuous manner with the composition of the samples. With increasing Cr and Se content of the samples containing H_2O the *a* axis decreases from 3·50 to 3·44 A., while the *c* axis increases from 25·5 to 26·8 A. By dehydration at 100° C. the *c* axis diminishes to 24·2 A., the *a* axis, however, remaining unchanged. At present it is not yet well established how the water is built into the crystal structure.

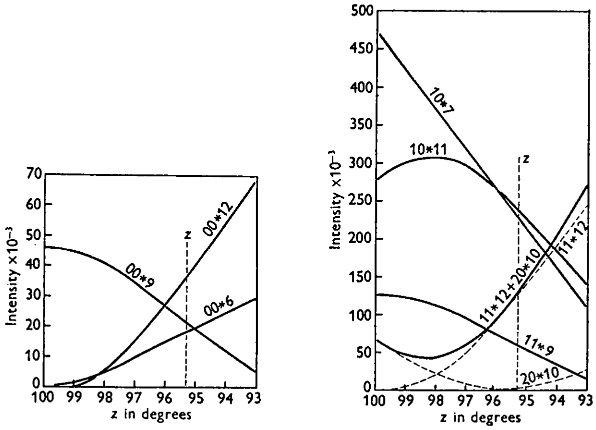

Fig. 1. Determination of the selenium parameter in sodium selenochromite, $NaCrSe_2$.

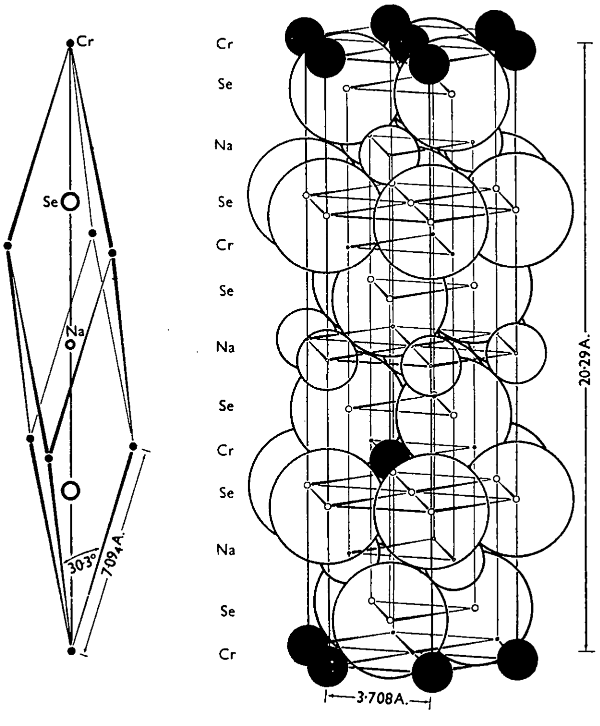

Fig. 2. The rhombohedral unit cell and the structure of sodium selenochromite, $NaCrSe_2$.

Intensity calculations for the compound $K_{0\cdot5}CrSe_2$ ($=KCrSe_2 . CrSe_2$) made it certain that the arrangement of successive layers is different from that of the compounds $NaCrS_2$, $KCrS_2$ and $NaCrSe_2$. In these compounds the succession of layers is that of cubic close-packing, while in the case of $KCrSe_2 . CrSe_2$ hexagonal- and cubic-packed layers are alternating, and hence the symmetry decreases to that of the space group C_{3v}^5–$R3m$.

Good rendering of the intensities was obtained with a parameter $z=141\cdot5°$ for the selenium ions. Hence the spacing Cr–Se is 2·46 A. (cf. 2·55 A. calculated from the Goldschmidt radii). The parameter *z* of the K ions could be determined only approximately to lie between 60 and 62°; with $z=61°$ the spacing K–Se would be 3·27 A. (calculated: 3·24 A.). The spacing Cr–Cr and Se–Se within the layers is 3·44 A. (calculated for Se^{2-}–Se^{2-} : 3·82 A.).

Rubidium selenochromite, $RbCrSe_2$

The rubidium compound was prepared by reaction of Cr_2Se_3 with Rb_2Se and selenium in the manner described above. It has the normal composition $RbCrSe_2$.

The X-ray powder photographs, which are very similar to those of the potassium compound with the exception of one weak line, permitted hexagonal rhombohedral indexing, giving the identity periods

$$I_a=3\cdot43 \text{ A. and } I_c=26\cdot9 \text{ A.}$$

The observed density is $d_f=5\cdot02$ g.cm.$^{-3}$, the calculated density is $d_x=5\cdot26$ g.cm.$^{-3}$ For this compound, also, an arrangement of successive layers as in $NaCrSe_2$ has definitely to be excluded. A final determination of the structure would require Weissenberg photographs.

Rubidium thiochromite, $RbCrS_2$

The compound $RbCrS_2$, prepared from Cr_2S_3, Rb_2S and sulphur in the same manner as the seleno compounds, was obtained only once in several experiments. The composition of the other samples showed considerable variations of the ratio Cr : S and made the existence of Cr II, III compounds appear probable, similar to the potassium thiochromites prepared after Schneider (1897). The compound $RbCrS_2$, like the other thio- and selenochromites, forms black, brilliant hexagonal disks. The X-ray powder photographs admit hexagonal indexing with $I_a=3\cdot39$ A. and $I_c=16\cdot20$ A. The space group and the atomic positions have not yet been determined.

Conclusion

It is remarkable that for the three selenochromites the *a* axis decreases from the sodium to the rubidium compound. In the structure the value of the *a* axis corresponds to the distance between neighbouring atoms within one layer. Hence the values of the radius of the Se^{2-} ion are 1·85 A. in $NaCrSe_2$, 1·72 A. in the potassium compound and $1\cdot71_5$ A. in $RbCrSe_2$. The contraction of the selenium ions in the direction of the layers can be explained by the polarization caused by the Cr^{3+} ions, which increases from $NaCrSe_2$ to $RbCrSe_2$, following the decreasing contrapolarizing action of the ions in the series Na^+—Rb^+.

Table 3. *Observed and calculated interionic spacings of the alkali selenochromites*

(All values in A.)

		$NaCrSe_2$		$K_{0.5}CrSe_2$		$RbCrSe_2$	
Spacing		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Alk.–Se		2·92	2·89	3·27	3·24	—	3·40
Cr–Se		2·55	2·55	2·46	2·55	—	2·55
Cr–Cr	within one layer	3·70	—	3·44	—	3·43	—
Se–Se		3·70	3·82	3·44	3·82	3·43	3·82
Alk.–Alk.		3·70	—	3·44	—	3·43	—

The mobility of the electrons of the selenium ions, which increases with the polarization, is manifested in the electric conductivity of the compounds. While $NaCrS_2$ is still nearly a non-conductor, the specific resistance measured on samples under a pressure of 1200 kg.cm.$^{-2}$ is 6·4 ohm-cm. for $NaCrSe_2$ and 0·2 ohm-cm. for $RbCrSe_2$. The conductivity of $RbCrSe_2$ is thus not much less than that of microcrystalline graphite.

In Table 3 the observed interionic spacings of the alkali selenochromites are compared with the values calculated from the Goldschmidt ionic radii.

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Indexing Powder Photographs of Tetragonal, Hexagonal and Orthorhombic Crystals

By R. Hesse

Chemical Institute of the University, Uppsala, Sweden

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A numerical method of indexing X-ray powder photographs without the use of single-crystal data is described. The method leads to a fairly systematic treatment of tetragonal and hexagonal photographs, and has also proved valuable in orthorhombic cases.

The indexing of powder photographs of tetragonal and hexagonal materials, which cannot be obtained in suitable single crystals, is most frequently carried out by means of the graphical methods of Hull & Davey (1921), Bjurström (1931), and of Bunn (1945, p. 133). These and other related graphical methods are, however, very time-consuming and are liable to fail in cases with a high proportion of missing reflexions. Some crystallographers might prefer to solve the problem numerically if practicable methods existed. The early numerical methods of Runge (1917) and of Johnsen & Toeplitz (1918), however, are mainly of theoretical interest and will generally not work in practice.

In the following, an account is given of a numerical method which has proved to be very successful in several practical tests carried out in Uppsala. It allows of a fairly systematic treatment of tetragonal and hexagonal cases. It has also been successful in ortho rhombic cases, although there the treatment will be less systematic. Earlier investigators may have applied similar methods to those of this paper, but a consistent account seems to be lacking.

1. TETRAGONAL AND HEXAGONAL (RHOMBOHEDRAL) SYSTEMS

1·1. General relations

In the tetragonal and hexagonal (rhombohedral) systems the quadratic forms are

$$\sin^2\theta=\frac{\lambda^2}{4}\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right)$$

and

$$\sin^2\theta=\frac{\lambda^2}{4}\left(\frac{4(h^2+k^2+hk)}{3a^2}+\frac{l^2}{c^2}\right),$$