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To cite this version:
P. Pieranski, E. Dubois-Violette, F. Rothen, L. Strzelecki. Geometry of Kossel lines in colloidal
 crystals. Journal de Physique, 1981, 42 (1), pp.53-60. <10.1051/jphys:0198100420105300>. <jpa-
 00208991>

HAL Id: jpa-00208991
https://hal.archives-ouvertes.fr/jpa-00208991
Submitted on 1 Jan 1981

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Geometry of Kossel lines in colloidal crystals

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(Reçu le 26 juin 1980, accepté le 18 septembre 1980)

1. Introduction. — The occurrence of Kossel lines in light diffraction pattern of colloidal crystals (C.C.) was reported recently by Clark, Hurd and Ackerson [1] and, independently by us [2].

In reference [1] the existence of Kossel lines was mainly interpreted as a qualitative indication of crystal perfection. In reference [2], where we were mainly concerned with the investigation of viscoelasticity of C.C., the Kossel lines were used as a probe of crystal deformation.

The purpose of the present paper is to reconsider Kossel lines in C.C. from a more general point of view. One can distinguish between two different aspects of the problem. The first aspect is the geometric characteristics of the diffraction pattern such as the shape of Kossel lines and their relative positions. It has an obvious importance in the determination of the crystalline structure. The second aspect is that of the light intensity profile of the individual Kossel lines and is related to the details of light diffraction at both the microscopic (polymer/solvent) and macroscopic (C.C./container) interfaces.

We will show in section 2.3 that, as far as the determination of the crystalline structure from the Kossel lines is concerned, the projection of the diffracted light on a spherical screen (as proposed in reference [2]) which were necessary to improve the quality of the diffraction image and to allow the measurements of the Kossel lines positions.

We show in section 5 a number of computer drawings representing the Kossel lines configurations for b.c.c. and f.c.c. colloidal crystals of different densities. The comparison with experimental results is made in section 6.

2. Geometry of Kossel lines. Principles. — The Kossel lines observed in colloidal crystals are analogous to Kossel lines in X-ray diffraction [3, 4] or to the Kikuchi [5] lines in electron diffraction experiments. The principle of their formation may be based on an elementary consideration such as that proposed in reference [3] which we report below with the necessary modifications:

2.1 Principles of Divergent Beam Diagrams [3]. — Let us suppose that a point source O of monochromatic light is situated inside the colloidal monocrystal (Fig. 1). Then let us consider a family of lattice planes \((hkl)\) and a light ray OA incident on these planes at the Bragg reflection angle \(\theta\) (for a given light wavelength \(\lambda\)). One expects that due to Bragg reflections the transmitted light intensity of the ray OA will be different from the intensity of other rays such as OB, which do not satisfy the Bragg condition. Other rays similar to OA, incident on the planes \((hkl)\) at the same Bragg angle \(\theta\), form the KOSSEL CONE, with the axis \([hkl]\) and cone angle \(\mu = \frac{\pi}{2} - \theta\).
2.2 CONSTRUCTION OF KOSSEL DIAGRAM. — The Kossel diagram is particularly simple when the projection screen is spherical and centred at point O (light source). In this case the intersections of the Kossel cones with the projection screen are circular. The systematic construction of the Kossel diagram proceeds as follows [3] (Fig. 2):

Let us consider the reciprocal lattice with the origin at point O and the sphere S of radius 2/λ (twice as large as Ewald sphere) centred at the same point O. The reciprocal lattice vector \( \mathbf{k}_{hkl} \) inside the sphere S, are shorter than the radius 2/λ. (In terms of the real space geometry that means that the interplanar spacing \( d_{hkl} \) is larger than \( λ/2 \) so that the Bragg reflections are possible on planes \( (hk\ell) \).) The corresponding Kossel line is the intersection of the sphere S with the plane \( P_{hkl} \) normal to \( \mathbf{k}_{hkl} \); the ray OA satisfies the Bragg relation as required.

2.3 CONSTRUCTION OF THE RECIPROCAL LATTICE FROM THE KOSSEL DIAGRAM. — It is pointed out in reference [3] that, theoretically, it is possible to determine the reciprocal lattice of the crystal from its Kossel diagram: the centre \( C_{hkl} \) (Fig. 2) of each Kossel line defines precisely the direction of the reciprocal lattice vector \( \mathbf{OK}_{hkl} \). The length \( \left| \mathbf{k}_{hkl} \right| \), equals to \( 1/d_{hkl} \) and is given by the angle \( μ \) of the corresponding Kossel cone.

In the case of X-ray or electron diffraction experiments, because of the short wavelength of the radiation many reciprocal lattice points are situated inside the Ewald sphere and according to the previous section the angle \( μ \) will be very large (close to π/2). In general, only a small portion of the Kossel diagram is available experimentally so that the determination of the axis \( \mathbf{OC}_{hkl} \) and of the angle \( μ_{hkl} \) is difficult [3]. In the case of light diffraction by the colloidal crystals we are often in very different conditions where only a few reciprocal lattice points are inside the sphere S and it is possible experimentally to obtain at least half of the whole Kossel diagram.

3. Light diffraction apparatus. — The experimental set-up with some modification is essentially the same as that used previously in the investigation of the viscoelastic properties of C.C. [2]. We observed that the refraction on the walls of the cylindrically shaped test tube affected the resolution of the Kossel diagram. In order to avoid this effect a portion of the test tube was cut off and replaced by a glass slide of good optical quality (Fig. 3).

The test tube T containing the sample is immersed in the spherical vessel V (10 cm in diameter) filled with water in order to minimize the refraction at sample/water interface. The external surface of the vessel V, except for small equatorial window W, was roughened with abrasive sand and used as a translucent screen for the Kossel diagram.

The He-Ne laser beam (5 mW) was incident on the C.C. sample through the window W. Its direction and the position of the sample were such that the illuminated area of the C.C. coincided with the centre O of the vessel V. Let us define the x-axis as a normal to the wall of the sample and the z-axis as vertical. Due to the ball bearing mounting of the test tube holder, the...
sample can rotate around the z-axis, so that the incidence angle \( \alpha \) between the laser beam and the x-axis can be changed. Only a part of the spherical screen is illuminated by the backscattered light. The illuminated area is a hemisphere defined by \( x > 0 \). The second hemisphere \( (x < 0) \) could be illuminated as well if the sample were transparent (thin) enough. However, in the case when the crystal has inversion symmetry the Kossel diagram on one hemisphere is enough to determine the crystal structure. In order to measure the angular position of Kossel lines on the projection sphere, a simple two angle goniometer was added to the original set-up. The azimuthal angle \( \varphi \) and the polar angle \( \theta \) can be measured with \( \pm 1^\circ \) accuracy.

4. Representation of Kossel diagrams. — 4.1 STEREOGRAPHIC AND ORTHOGONAL PROJECTION. — The set \( \{ C_{kl} \} \) of Kossel lines centres is identical to the set of POLES of SPHERICAL PROJECTION of the crystal faces as defined in reference [7]. The conventional planar representation of the spherical projection is obtained by its STEREOGRAPHIC PROJECTION (Fig. 4a).

Let \( \mathbf{R}(x, y, z) \) be a vector between the centre \( O \) and an arbitrary point \( R \) on the projection sphere. The vector \( \mathbf{R}_s(y, z) \) is by definition the result of the ORTHOGONAL PROJECTION of \( \mathbf{R} \) into the plane \( (y, z) \) (Fig. 4b).

4.2 PRACTICAL CHOICE BETWEEN THE STEREOGRAPHIC AND ORTHOGONAL PROJECTION. — The experimental study of the light diffraction pattern can be done in three different ways:

1) By goniometric measurements of the Kossel lines position.

2) By taking the photographic picture of the Kossel diagrams.

3) By a direct visual inspection of the Kossel diagram.

The goniometric results can easily be used to construct both the stereographic and orthogonal projection. The stereographic projection of the set \( \{ C_{kl} \} \) would have the advantage of conserving the angular relationships between the points \( C_{kl} \). If the stereographic projection were applied to the whole Kossel diagram, the Kossel lines would remain circular but their diameter would change as a function of their distance from the centre (x-axis). For the distance between the camera (or eye) and the spherical screen large enough, the photographic (or retinal) image is in fact an orthogonal projection of the Kossel diagram on the plane of the film (or of the retina). For the practical purpose of the crystal structure identification, the direct, naked eye inspection is sufficient in most cases. Also, the characteristic features of the Kossel diagram allow us to estimate directly the density of the crystal.

The goniometric measurements are necessary when this density must be known more precisely.

Our conclusion is that, for the practical purpose of crystal structure identification, the orthogonal projection is well adapted. The computer drawings of the Kossel diagrams shown in section 5 are made using this convention.

4.3 REFRACTION CORRECTIONS [10]. — The refractive index of the C.C. can be estimated as follows [6]:

\[
n_{\text{C.C.}} = \phi_w n_w + \phi_{ps} n_{ps}
\]

where \( \phi_w \) and \( \phi_{ps} \) are the volume fractions of the solvent (water) and of the polymer (polystyrene). The index of water at 20 °C is \( n_w = 1.33 \) while that of polystyrene is \( n_{ps} = 1.6 \) [6].

In all our samples (and in the most common cases) the polystyrene fraction in the C.C. is less than 10% so that the ratio \( n_{\text{C.C.}}/n_w \) is smaller than 1.02.

Let us call \( \beta_{\text{C.C.}} \) the incidence angle which the light ray \( \mathbf{R}_{\text{C.C.}} \) propagating in C.C., makes with the container wall (Fig. 5). The angle \( \beta_w \) of the refracted ray \( \mathbf{R}_w \) in water is given by

\[
\cos \beta_w = \frac{n_{\text{C.C.}}}{n_w} \cdot \cos \beta_{\text{C.C.}}
\]
the refraction angle $\Delta \beta = \beta_{\text{C.C.}} - \beta_w$, which is important for small angles $\beta$, may be approximated by

$$\Delta \beta \approx 2 \left( \frac{n_{\text{C.C.}}}{n_w} - 1 \right) |(\beta_w + \beta_{\text{C.C.}})/2| \leq 25^\circ.$$  

With $\left( \frac{n_{\text{C.C.}}}{n_w} - 1 \right) \leq 0.02$ one calculates that $\Delta \beta \geq 3^\circ$ for $(\beta_w + \beta_{\text{C.C.}})/2 \leq 25^\circ$.

In orthogonal projection the length $|R_\perp|$ of the vector $R_\perp$ is $|R| \cdot \cos \beta_w$. Using equation (2) one gets

$$|R_\perp| = \frac{n_{\text{C.C.}}}{n_w} \cdot |R| \cdot \cos \beta_{\text{C.C.}}.$$  

This equation means that the orthogonal projection of the Kossel diagram obtained experimentally is dilated by a factor $n_{\text{C.C.}}/n_w$ as compared with the theoretical one (Fig. 5).

The refraction effects in the stereographic projection must be calculated separately for different incidence angles.

5. **Kossel diagrams — theoretical.** — As we will see in next section our C.C. samples always crystallized either in b.c.c. or in f.c.c. structures. Thus, we have drawn a series of Kossel diagrams for both structures for a number of different densities.

5.1 **Drawing program features.** — The drawings were made using the CRDS (LS-11 based) computer with an output on Screen of the Tektronix Terminal 4010-1.

The program is interactive so that the drawings can be elaborated progressively on the Terminal Screen and then, if satisfying, can be output on Versatec 1600 electrostatic plotter-printer.

Another feature of the program is that the whole Kossel diagram can be rotated around x, y and z-axis, defined as follows: the x-axis is chosen to be perpendicular to the drawing plane. The z-axis is vertical. Such a choice corresponds to the experimental conditions, where the x-axis was defined as a normal to the container wall and the available part of the Kossel diagram corresponded to $x > 0$ hemisphere.

The experimental points, measured with the goniometer, can be plotted on the Kossel diagram and compared with the theoretical predictions.

5.2 **B.C.C. structure.** — The series of drawings in figure 6 shows how a Kossel diagram develops when crystal density is lowered. The sphere $S$ was chosen to have the diameter $2n_{\text{C.C.}}/\lambda$ where $n_{\text{C.C.}} = 1.4$ is the approximate value of the refractive index, while $\lambda = 6328 \, \text{Å}$ is the wavelength of the laser beam. For the density $N > N_{\text{max}}^{\text{b.c.c.}} = 61.3 \times 10^{12} \, \text{part/cm}^3$ all reciprocal lattice points are situated outside the sphere $S$ and no Kossel lines are possible. For $N = 60 \times 10^{12} \, \text{part/cm}^3$ the (110) reciprocal lattice points, which are the closest to the origin $O$ (Fig. 2), enter into the sphere $S$. The corresponding Kossel diagram is drawn in figure 6a. The crystal orientation in this drawing was chosen in such a way that the (110) Kossel line is centred around $x$-axis. As we will see...
in section 6.2 such orientation of the crystal is usually imposed by the boundary conditions at container walls. The diameter of a Kossel line increases for successive dilutions; in figure 6b for \( N = 40 \times 10^{12} \text{ part/cm}^3 \) the neighbouring Kossel lines became tangent. In order to visualize better the symmetry elements of this diagram two other drawings (Fig. 6c and 6d) were made for the same density. In figure 6c the b.c.c. crystal is oriented with the [111] axis parallel to x-direction; the three-fold symmetry of the diagram is evident.

In figure 6d the four-fold symmetry of the [100] axis is shown. Further dilution \( (N = 21 \times 10^{12} \text{ part/cm}^3) \) results simultaneously in the intersection of the four Kossel cones along the [100] (or [010] and [001]) axis and in appearance of new Kossel line centred around this [100] axis. One of the characteristic features of this new configuration (Fig. 6e) is the occurrence of points where three Kossel lines intersect.

For \( N = 11.5 \times 10^{12} \text{ part/cm}^3 \) (200) and (011) lines became tangent and then intersect. The (211) line appears at the intersection (Fig. 6f).

5.3 F.C.C. STRUCTURE. — The corresponding series of Kossel diagram is shown in figure 7. The shortest reciprocal lattice vectors are of (111) type so that the corresponding (111) Kossel lines appear first on the diagram for \( N = N_{\text{max}} = 66.7 \times 10^{12} \text{ part/cm}^3 \) (Fig. 7a, \( N = 50 \times 10^{12} \text{ part/cm}^3 \)). The crystal orientation in this drawing was chosen in a way that the point \((C_{111})\) is in the centre. As we will see in section 5.5 this choice corresponds to the experimentally observed crystal orientation at the container wall.

For appropriate crystal dilution (200) lines appear on the diagram. The (111) and (200) lines become tangent for \( N = 36.6 \times 10^{12} \text{ part/cm}^3 \) (Fig. 7b).

Then, the (200) lines become tangent and intersect along the [110] axis which is a centre of new (220) line \( (N = 15 \times 10^{12} \text{ part/cm}^3) \) (Fig. 7c).

For the density \( N = 10 \times 10^{12} \text{ part/cm}^3 \) these new (220) lines become tangent and then for \( N = 9.4 \times 10^{12} \text{ part/cm}^3 \) they intersect the (111) lines. New (131) lines appear at the intersection.

The second order reflections take place on (111) planes for \( N \leq 8 \times 10^{12} \text{ part/cm}^3 \). As a result (222) line appears in the centre (around [111] axis) (Fig. 7e).

The diagram of figure 7f shows that the triple intersection points observed previously in figure 7e exist also for smaller densities \( (N = 6 \times 10^{12} \text{ part/cm}^3) \).

6. Experimental results. — 6.1 PREPARATION OF SAMPLES A AND B. — Two different polystyrene colloids were synthesized using emulsion polymerization technique. The diameters of the polystyrene particles as determined by the electron microscopy were respectively \( d_A = 1.090 \text{ Å} \) and \( d_B = 2.450 \text{ Å} \). Two series of colloidal crystals were prepared by appropriate dilution in water of the original suspensions and by successive purification using the ionic exchange resin Amberlite MB-3.

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Fig. 7. — Series of Kossel diagrams produced by f.c.c. crystals of decreasing density. (In figures d, e, f some (111)-type lines were omitted for simplicity.)

Fig. 8. — Structure of interfacial layer (b.c.c. structure): a) random orientation; b) oriented by shear flow. Crystallites are oriented with (110) plane parallel to the drawing plane. The parallel lines in crystallites indicate the orientation of (1, 1, 0) planes.
At the original concentration sample A showed blue reflections for normal light incidence conditions and no Kossel lines were observed in the light diffraction apparatus. In order to obtain the first Kossel lines the original sample A was diluted by a factor of 3.

The original concentration of sample B was low enough for the occurrence of Kossel lines.

6.2 Boundary conditions. — The general feature of Kossel diagrams obtained with all samples A and B was that there was always at least one Kossel cone with its axis along the normal to the container wall (x-axis in Fig. 3a). On the other hand, it was evident from microscopic observations [8] that the samples were polycrystalline with crystallites (~10-100 μm) smaller than the area illuminated by laser beam (~1 mm²).

We concluded that the crystallites which are in contact with the container wall are always oriented with the same crystal face parallel to it.

The crystallite orientation in the yz plane was random immediately after the sample was introduced to the test tube; no Kossel lines other than the central one were present.

6.3 Monocrystal diagrams. — We found that an efficient way to remove the degeneracy of orientation in yz plane, is to apply a shear deformation larger than the elastic limit by a sudden rotation of the whole sample around z-axis. Even if our experimental conditions are different from those of reference [1], we think that our observations agree with those of Clark, Hurd and Ackerson [1], [9].

6.3.1 Sample A — b.c.c. structure. — The Kossel diagram obtained after the application of the shear deformation, shown in figure 9b, in a superposition of two simpler diagrams, shown in figures 9a and 9c, which can be identified individually as produced by b.c.c. crystals oriented in different way. The relative orientation of Kossel diagrams in figures 9a and 9c in that of twin b.c.c. crystals with (112) composition plane parallel to the shear plane (Fig. 10). A more detailed study of the twinning mechanism is postponed to another article.

When the sample is allowed to anneal, the size of twin crystallites grows and it is possible to obtain separately the two diagrams by a careful focusing of the incident laser beam. In figure 11 we show a photograph of the Kossel diagram produced by one large monocrystal.

Even if the identification of the b.c.c. structure is possible directly by a visual investigation of the characteristics of the Kossel diagram, a more quantitative test was done by measuring the Kossel line positions using the goniometer. The experimental points were then plotted on the computer monitor screen. Using the interactive facility of the drawing program, a best fit of the Kossel diagrams with the experimental points was achieved by appropriate choice of the b.c.c. crystal density and orientation (shown in Fig. 12).

6.3.2 Sample B — f.c.c. structure. — In sample B the shear deformation effect was also partially to remove the degeneracy of crystallite orientation in plane yz. The Kossel diagram immediately after the application of the shear deformation was a superposition of two independent contribution shown in figure 13.

As in the case of sample A, after annealing, the crystallite size was large enough to obtain the separate
diagrams shown in figures 13a and 13b. The identification of the f.c.c. structure from characteristic features of the Kossel diagrams was confirmed by the goniometric measurements.

In figure 14 we show the experimental points superposed on a Kossel diagram characteristic of an f.c.c. crystal, oriented with [111] axis parallel to the x-direction.

6.4 Diagrams of diluted samples. — 6.4.1 Samples A. — In the case of samples A for concentrations lower than \(N_{\text{min}}^A = 20 \times 10^{12} \text{ part/cm}^3\) the crystalline structure was no more recovered despite the addition of the ionic exchange resin. Probably, due to the commercial grade quality of the resin used in the experiments, polyelectrolyte impurities were introduced into the sample with the resin. At low crystal densities this contamination made impossible the recrystallization of the samples.

For densities ranging between \(N_{\text{min}}^B = 2 \times 10^{12} \text{ part/cm}^3\) and \(N_{\text{max}}^B\) the Kossel diagrams of purified samples were of b.c.c. type. When diluted gradually, their evolution exactly followed the theoretical previsions shown in figure 6.

6.4.2 Samples B. — Samples B, made of larger particles provided good Kossel diagrams for concentration as low as \(N_{\text{min}}^B = 2 \times 10^{12} \text{ part/cm}^3\). At concentrations higher than \(N_{\text{max}}^B = 30 \times 10^{12} \text{ part/cm}^3\) the suspensions became very viscous. As a consequence, the ordering by shear deformation and successive annealing of the polycrystalline sample was less efficient and it was difficult to obtain satisfactory diagrams. For concentrations intermediate between \(N_{\text{max}}^B\) and \(N_{\text{min}}^B\) the observed Kossel diagrams were that shown in figure 7.

6.5 Phase coexistence. — In samples A, we observed the phase coexistence between the f.c.c. and b.c.c. structures. This phenomenon takes place only in
very particular conditions where, due to the introduction of ionic impurities to the sample, the resulting temperature of the C.C. is very low (~ 40 °C).

The phase coexistence was deduced both from analysis of the Kossel diagrams and from microscopic observations.

In Kossel diagrams two central lines of slightly different diameters were observed (Fig. 15). Theoretically, the diameters of the central Kossel lines (110) and (111) are different in b.c.c. and f.c.c. structure for the same crystal density. If one supposes that in a polycrystalline sample two kinds of crystallites are present, then the Kossel diagram will show two central lines of different diameters as observed.

The shear deformation, applied to such a sample, destroyed the f.c.c. structure.

7. Conclusions. — We have shown experimentally that colloidal crystals offer the unique opportunity to obtain easily a HALF (or even the TOTALITY) of the Kossel diagram by a simple light diffraction experiment.

Using such large angle Kossel diagrams we have shown how to determine (1) the structure, (2) the orientation and (3) the density of colloidal crystal. Also, we have shown previously that the Kossel lines can be used to monitor the crystal deformation (Ref. [2]).

The experimental set-up described in this paper can be perfected by using samples of an appropriate thickness to give simultaneously both the backscattered and the transmitted light patterns.

We intend to report, in the near future, results concerning the twinning mechanism and phase coexistence in C.C.

Acknowledgments. — We greatly acknowledge Professors D. Taupin, C. Young, R. Steineman and S. Lagerwaal for valuable discussions on Kossel and Kikuchi lines. One of us (P. P.) is indebted to Professor R. Meyer for his invitation at Brandeis University where a part of this work was done. The computer drawings were made with the kind collaboration of Mr. F. Lonberg and Mr. V. Taratuta. We thank Mr. D. Argentini for technical assistance and Miss D. MacKnight for critical reviewing and typing of the text.

We acknowledge the referee remarks concerning light diffraction in C.C.

References

[10] The calculations of light intensity for Kossel lines would involve an effective refractive index which is a complex function of wave vector, rather than a constant given by eq. (1). For the purpose of the present paper, where we are interested only in geometry of Kossel diagram, we believe the approximation (1) to be accurate.