DETERMINING ORIENTATIONS IN METALS OF HEXAGONAL CRYSTAL STRUCTURE BY ETCH PIT FIGURES

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For determining orientations in metal crytals Laue's X-ray, back reflection method is mostly prevalent. In polycrystalline metals, however, determination by Laue's technique is only possible in case the diameter of the crystallites is greater than that of the X-ray beam. Upon decreasing beam diameter the exposure time will increase which will result in a cumbersome procedure, not even mentioning difficulties inherent in using a thin X-ray beam.

The exposure time of one Laue film for a 0.1 mm diameter X-ray beam is 8 to 12 hours depending on experimental circumstances.. Even by such thin X-ray beams orientations only in crystallites corresponding to ASTM grade 4 can be determined, since the respective particle diameter is 0.091 mm. Determining orientations even in such coarse grained material is, however, so labour consuming that the orientation determination of all crystallites in a 100×100 mm^2 viewing area with an enlargement of 1 : 100 would require 100 days. The time of evaluation should be added which for an experienced analyst would take 10 days. Hence it is the extraordinary labour consumption which is the reason why no researchers are concerned with tasks connected to the solution of orientations in polycrystalline metals in most cases. Thus for solving problems of this character another way should be sought for.

Determining dislocation density by the etch pit method is becoming more and more prevalent in the last two or three decades. The essence of this procedure is that a carefully prepared metallographical surface is attacked only on certain definite points by special etching reagents. These points define the etch pit figures and are assumed to be the intersection points of dislocations and the etched surface [1—3].

In the course of producing etch figures several etching reagents have been developed that etch pits bordered by planes of specified $(h'k'l')$ indices. If a crystal is placed into the proper solvent or etching reagent those regions which possess excess free energy dissolve at a faster rate than the rest. Thus, sooner or later, etch pit figures will form in the crystal surface bordered by planes of specified crystal indices. Their geometry will only depend on the

(*hkl*) indices of the metallographic surface in which the etch figures were formed. Etch figures of this kind are seen in the surface of a CdS crystal in Figs 1 and 2.
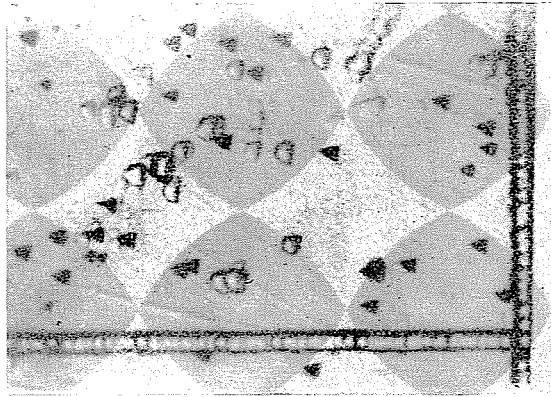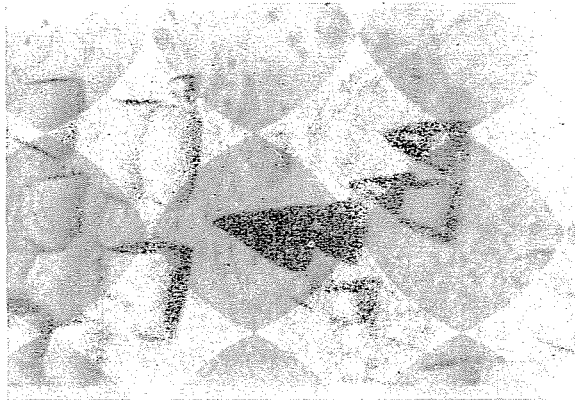

Fig. 1

Fig. 2

It can be observed from those figures that the etch figures of the crystal are of well defined geometry. Now in the following we shall proceed to show that if an etching reagent is known such that will etch pits bordered by specified {*hkl*} crystallographic planes for a material of hexagonal structure, then it is possible to determine the Miller indices of the metallographical surface, i.e., the orientation of the crystal using etch figure data.

Before introducing details of the procedure delineated above it is worth to note that for determining orientations of cubic crystals several authors used geometric data of etch figures [5]. This can also be solved — as we shall see it in the following — for hexagonal crystals.

Let the etch pit be a triangle-based pyramid as in Fig. 3 with its base as the orientation (HKL) tested, its sides bordered by $(H_1K_1L_1)$, $(H_2K_2L_2)$, and $(H_3K_3L_3)$ crystallographic indices. The indices of the crystallographic plane (HKL) should be determined. (Thus far, and further on as well, upper case indices refer to hexagonal, while others in lower case to either general or to cubic crystallographic system.)
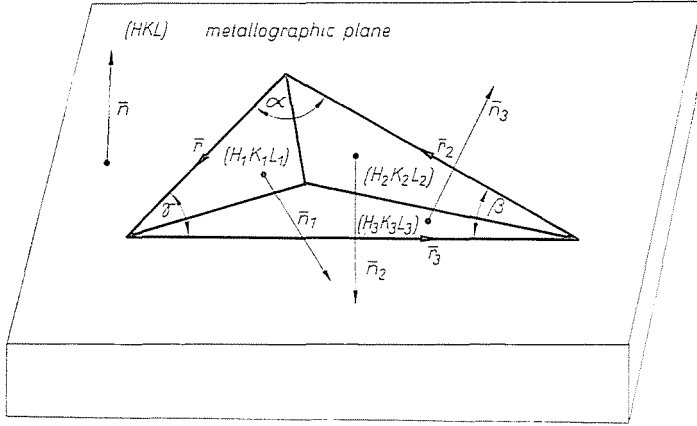

Fig. 3

Let vectors perpendicular to the side planes of the etch pit be $\bar{\mathbf{n}}_1$, $\bar{\mathbf{n}}_2$, and $\bar{\mathbf{n}}_3$, while $\bar{\mathbf{n}}$ be the normal of the tested crystallographic plane. Provided the preceding three normals are known, $\bar{\mathbf{n}}$ can be determined as the vector product of two arbitrary intersection lines of the etch figure, considering that an intersection line is a cut between the plane of sample and the side plane of the pit.

Hence the $\bar{\mathbf{n}}_1$ normals in, vector product with the normal of a plane parallel to the plane of sample will just give the intersection lines in question. Using notation in Fig. 3

$$\bar{\mathbf{n}}_1 \times \bar{\mathbf{n}} = \bar{\mathbf{r}}_1$$

$$\bar{\mathbf{n}}_2 \times \bar{\mathbf{n}} = \bar{\mathbf{r}}_2$$

or

$$\bar{\mathbf{n}}_3 \times \bar{\mathbf{n}} = \bar{\mathbf{r}}_3$$

The cosines of angles α, β, and γ as marked in Fig. 3 are given as the scalar products of the vectors of appropriate intersection lines as

$$\cos \alpha = \frac{-\,\bar{\mathbf{r}}_2 \cdot \bar{\mathbf{r}}_1}{|\bar{\mathbf{r}}_2| \cdot |\bar{\mathbf{r}}_1|}$$

$$\cos \beta = \frac{-\,\bar{\mathbf{r}}_2 \cdot \bar{\mathbf{r}}_3}{|\bar{\mathbf{r}}_3| \cdot |\bar{\mathbf{r}}_2|}$$

$$\cos \gamma = \frac{-\,\overline{\mathbf{r}}_3 \cdot \overline{\mathbf{r}}_1}{|\overline{\mathbf{r}}_3| \cdot |\overline{\mathbf{r}}_1|}.$$

In the last three equations values of the left sides can be determined from the shape of the etch figures by measurement. This way, according to the equations above, the (HKL) indices sought for can be calculated.

The calculation is but slightly complicated by the problem that for given $(H_1 K_1 L_1)$, $(H_2 K_2 L_2)$, and $(H_3 K_3 L_3)$ planes in a hexagonal system it is not so easy to assign their normal vectors as in the cubic system. Therefore, we give some relationships which provide the normal vectors belonging to an arbitrary (HKL) plane.

For all ideal crystals the vectorial relation

$$\overline{\mathbf{r}} = \overline{\mathbf{r}}_0 + m\overline{\mathbf{a}} + n\overline{\mathbf{b}} + p\overline{\mathbf{c}}$$

holds, where $\overline{\mathbf{r}}$ and $\overline{\mathbf{r}}_0$ are vectors marking points of the same kind in the crystal. If m, n, and p are integers then $\overline{\mathbf{a}}$, $\overline{\mathbf{b}}$, and $\overline{\mathbf{c}}$ will be the translational unit vectors characteristic to the crystallographic system.

Thus an arbitrary $\overline{\mathbf{r}}$ vector also signifies a line parallel to some crystallographic direction. If numbers m, n, and p are the smallest possible integers, from innumerable possibilities, those are exactly the indices of the crystallographic directions which in square brackets [ ] are used for describing the appropriate crystallographic directions.

In a similar way the relation for an arbitrary crystallograhic plane can be given as:

$$(\overline{\mathbf{r}} - \overline{\mathbf{r}}_0)\,\overline{\mathbf{n}} = 0$$

where $\overline{\mathbf{r}}_0$ and $\overline{\mathbf{r}}$, respectively, mark a specified and an arbitrary point of a crystallographic plane in question, while $\overline{\mathbf{n}}$ is the normal of the same plane.

In the cubic crystallographic system a (hkl) plane is always perpendicular to the hkl direction, in non-cubic systems, that, however, is only maintained under special conditions.

In the hexagonal system $\overline{\mathbf{a}}$, $\overline{\mathbf{b}}$, and $\overline{\mathbf{c}}$ translational vectors are related as follows

$$|\overline{\mathbf{a}}| = |\overline{\mathbf{b}}| \neq |\overline{\mathbf{c}}|$$

and

$$\frac{\overline{\mathbf{a}} \cdot \overline{\mathbf{b}}}{|\overline{\mathbf{a}}| \cdot |\overline{\mathbf{b}}|} = -\frac{1}{2} \quad \text{and} \quad \overline{\mathbf{b}} \cdot \overline{\mathbf{c}} = \overline{\mathbf{c}} \cdot \overline{\mathbf{a}} = 0$$

In other words, vectors $\overline{\mathbf{a}}$ and $\overline{\mathbf{b}}$ are of equal magnitude and include an angle of $120°$, whereas the magnitude of vector $\overline{\mathbf{c}}$ is different from the previous two ones, but perpendicular to those.

Provided $\overline{\overline{\mathbf{n}}}$ crystallographic direction perpendicular to (HKL) plane, or the indices of a crystallographic plane perpendicular to an arbitrary $[HKL]$

line are known in a hexagonal system, then it is possible to determine the orientation of crystals in a hexagonal crystallographic system on the basis of etch figure geometry, a task we have previously outlined.

Let $\overline{v}$ be a crystallographic direction given by the vectorial equation

$$\overline{v} = H\overline{a} + K\overline{b} + L\overline{c}$$

in the hexagonal system, furthermore vector $\overline{r}$ of a cubic system be parallel to vector $\overline{v}$ defined by

$$\overline{r} = h\overline{e}_1 + k\overline{e}_2 + l\overline{e}_3$$

It is evident from Fig. 4 that
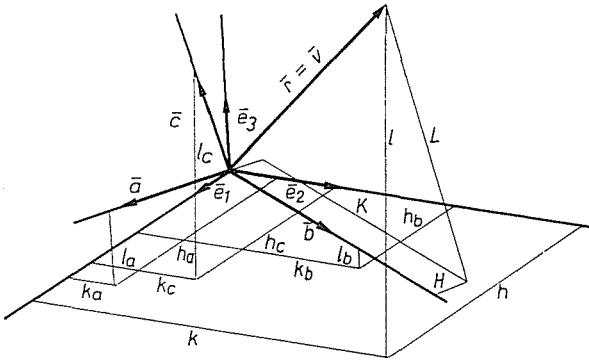
Fig. 4

$$\overline{a} = h_a\overline{e}_1 + k_a\overline{e}_2 + l_a\overline{e}_3$$

$$\overline{b} = h_b\overline{e}_1 + k_b\overline{e}_2 + l_b\overline{e}_3$$

$$\overline{c} = h_c\overline{e}_1 + k_c\overline{e}_2 + l_c\overline{e}_3$$

and

$$\overline{v} = H(h_a\overline{e}_1 + k_a\overline{e}_2 + l_a\overline{e}_3) + K(h_b\overline{e}_1 + k_b\overline{e}_2 + l_b\overline{e}_3) + L(h_c\overline{e}_1 + k_c\overline{e}_2 + l_c\overline{e}_3)$$

or

$$\overline{r} = (Hh_a + Kh_b + Lh_c)\overline{e}_1 + (Hk_a + Kbk_b + Lk_c)\overline{e}_2 + (Hl_a + Kl_b + Ll_c)\overline{e}_3$$

where components parallel to the unit vectors $\overline{e}_i$ are either components of vector $\overline{v}$ or vector $\overline{r}$. The expression may simply be written in matrix form

$$\overline{r} = A\overline{v}$$

or

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} h_a & h_b & h_c \\ k_a & k_b & k_c \\ l_a l_b & & l_c \end{bmatrix} \begin{bmatrix} H \\ K \\ L \end{bmatrix}$$

On the strength of the above mentioned, the corresponding hexagonal vector of a cubic system vector can be calculated without difficulty from the relationship

$$\bar{\mathbf{v}} = A^{-1}\bar{\mathbf{r}}.$$

Calculation is especially simplified if the relation between the co-ordinate systems is properly chosen. Hence, for example, in case of vectors $\bar{\mathbf{b}}$ and $\bar{\mathbf{c}}$ being parallel to unit vectors $\bar{\mathbf{e}}_2$ and $\bar{\mathbf{e}}_3$, respectively, then the matrix of tensor A becomes

$$A = \begin{bmatrix} \dfrac{a\sqrt{3}}{2} & 0 & 0 \\ -\dfrac{a}{2} & a & 0 \\ 0 & 0 & c \end{bmatrix}$$

and that of the inverse matrix

$$A^{-1} = \begin{bmatrix} \dfrac{2\sqrt{3}\,c}{3} & \dfrac{\sqrt{3}\,c}{3} & 0 \\ 0 & c & 0 \\ 0 & 0 & a \end{bmatrix}$$

It is seen that a correspondence can be established between cubic crystallographic directions $[hkl]$ and those $[HKL]$ of a hexagonal system, thus after conversion, relations between directions of the hexagonal system are as simple as in the cubic system.

Now, there remains only one problem to be solved, to determine the orientation from etch figures, namely to decide which (HKL) crystallographic plane is perpendicular to any crystallographic direction, or to show which (HKL) hexagonal system plane corresponds to any (hkl) plane in the cubic system and vice versa.
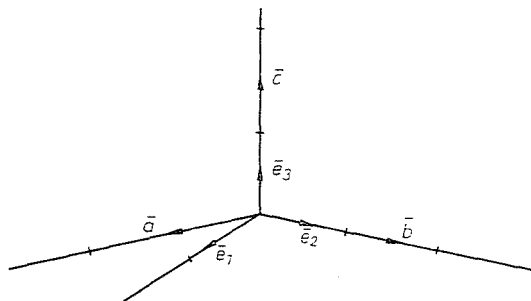

Fig. 5

According to Fig. 6, for an arbitrary (HKL) crystallographic plane three points $\dfrac{1}{H}$, $\dfrac{1}{K}$, and $\dfrac{1}{L}$, or vectors $\bar{\rho}_1$, $\bar{\rho}_2$, and $\bar{\rho}_3$ marking those points are known in a hexagonal system. Thus

$$\bar{\rho}_1 = \frac{1}{H}\,\bar{\mathbf{a}}, \qquad \bar{\rho}_2 = \frac{1}{K}\,\bar{\mathbf{b}}, \qquad \bar{\rho}_3 = \frac{1}{L}\,\bar{\mathbf{c}}.$$
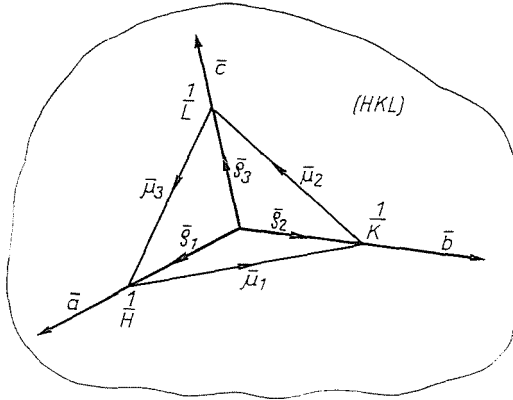

Fig. 6

The difference of any two out of these three vectors is in the crystallographic plane in question. Let these three be marked by $\bar{\mu}_1$, $\bar{\mu}_2$, and $\bar{\mu}_3$.
Then

$$\bar{\mu}_1 = \bar{\rho}_2 - \bar{\rho}_1 = \frac{1}{K}\,\bar{\mathbf{b}} - \frac{1}{H}\,\bar{\mathbf{a}}$$

$$\bar{\mu}_2 = \bar{\rho}_3 - \bar{\rho}_2 = \frac{1}{L}\,\bar{\mathbf{c}} - \frac{1}{K}\,\bar{\mathbf{b}}$$

or

$$\bar{\mu}_3 = \bar{\rho}_1 - \bar{\rho}_3 = \frac{1}{H}\,\bar{\mathbf{a}} - \frac{1}{L}\,\bar{\mathbf{c}}$$

The vector product of any two o the latters gives vector $\bar{\mathbf{n}}$ i.e.

$$\bar{\mathbf{n}} = \bar{\mu}_1 \times \bar{\mu}_2 = \bar{\mu}_2 \times \bar{\mu}_3 = \bar{\mu}_3 \times \bar{\mu}_1$$

$$\bar{\mathbf{n}} = \begin{bmatrix} \bar{\mathbf{e}}_1 & \bar{\mathbf{e}}_2 & \bar{\mathbf{e}}_3 \\ \left(\dfrac{h_a}{H} - \dfrac{h_c}{L}\right) & \left(\dfrac{k_a}{H} - \dfrac{k_c}{L}\right) & \left(\dfrac{l_a}{H} - \dfrac{l_c}{L}\right) \\ \left(\dfrac{h_b}{K} - \dfrac{h_a}{H}\right) & \left(\dfrac{k_b}{K} - \dfrac{k_a}{H}\right) & \left(\dfrac{l_b}{K} - \dfrac{l_a}{H}\right) \end{bmatrix}$$

Evaluating the vector product we obtain

$$\bar{n} = \left[H(k_b l_c - k_c l_b) + K(k_c l_a - k_a l_c) + L(k_a l_b - k_b l_a)\right] \bar{e}_1 +$$
$$+ \left[H(h_c l_b - h_b l_c) + K(h_a l_c - h_c l_a) + L(h_b l_a - h_a l_b)\right] \bar{e}_2 +$$
$$+ \left[H(h_b k_c - h_c k_b) + K(h_c k_a - h_a k_c) + L(h_a k_b - h_b k_a)\right] \bar{e}_3$$

this can be written as

$$\bar{n} = B \bar{\rho}$$

or

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} k_b l_c - k_c l_b & k_c l_a - k_a l_c & k_a l_b - k_b l_a \\ h_c l_b - h_b l_c & h_a l_c - h_c l_a & h_b l_a - h_a l_b \\ h_b k_c - h_c k_b & h_c k_a - h_a k_c & h_a k_b - h_b k_a \end{bmatrix} \begin{bmatrix} H \\ K \\ L \end{bmatrix}$$

Here vector

$$\bar{\rho} = H\bar{a} + K\bar{b} + L\bar{c}$$

should be considered as an auxiliary vector enabling to determine the perpendicular direction to the (HKL) crystal plane in the cubic system and its corresponding crystallographic plane. On solving this problem another question arises, namely, which (HKL) hexagonal system plane corresponds to a given cubic system plane. This is given as

$$\bar{\rho} = B^{-1} \bar{n}.$$

Here auxiliary vector $\bar{\rho}$ has three $[HKL]$ indices which are identical to the indices of the hexagonal crystallographical plane sought for.

Simplifying calculations we should consider relations given in Fig. 5, thus the latter expressions are reduced to

$$\bar{n} = B \bar{\rho}$$

or

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} 1 & \dfrac{1}{2} & 0 \\ 0 & \dfrac{\sqrt{3}}{2} & 0 \\ 0 & 0 & \dfrac{a}{c}\dfrac{\sqrt{3}}{2} \end{bmatrix} \begin{bmatrix} H \\ K \\ L \end{bmatrix}$$

similarly as the expression of hexagonal plane indices

$$\bar{\rho} = B^{-1} \bar{n}$$

corresponding to

$$
\begin{bmatrix} H \\ K \\ L \end{bmatrix} = \begin{bmatrix} \dfrac{\sqrt{3}}{2} & 0 & 0 \\ -\dfrac{1}{2} & 1 & 0 \\ 0 & 0 & \dfrac{c}{a} \end{bmatrix}
$$

Hence, all relations have been given for determining orientations in crystalline surfaces on the basis of etch pit figures of hexagonal crystals.

The author considers it to be his pleasant obligation to thank his colleagues Ödön Lendvai and György Andor that they were so kind as to have made Figs 1 and 2 available from their research work on CdS single crystals.

Summary

A method has been presented for determining crystal orientations in metals of hexagonal structure that is based on etch pit figures. When some solvent forms pits in the crystal surface which are bordered by crystal planes of the same kind on all sides, then the (*hkil*) Miller indices of the plane parallel to the surface can be determined from measured data of angles produced by intersection lines of etch figures and the surface plane of the sample. Provided that an appropriate etching reagent is available this procedure is also suitable for orientation determination of individual crystallites in polycrystalline metals, in cases where the X-ray method is already practically useless.

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