

# Crystal form and crystal structure

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teristic is based on a two carrier model by Ashley and Milnes, which is consistent with all experimental results.

### V. Acknowledgments

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## Crystal Form and Crystal Structure

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(19. IV. 68)

*Abstract.* The observed geometry and frequency of occurrence of the forms of crystals of a given species (barite) are cast in the form of a weighted reciprocal lattice. Fourier transform yields crude electron density maps with some details of the structure. The proportionate specific surface energies of the forms derived from the observed distribution in geological time and space, show significant agreement with the calculated potential energies (structure factors) associated with appropriate reciprocal lattice points.

The relationship of the crystal form to a periodic internal structure was discussed quantitatively by BRAVAIS [1] who related the planes of cleavage and the planes of

greatest morphological prominence to the planes of greatest net reticular density of lattice points (greatest interplanar spacing,  $d_i$ ). Then, if specific surface energy,  $\sigma_i$ , is inversely proportional to morphological importance;

$$\sigma_i = -k/d_i. \quad (1)$$

Considering only the cleavage, it is intuitively probable that the most widely separated planes should be the most probable cleavage planes. DONNAY and HARKER [2] pointed out that space group symmetry elements change the areal densities of morphologically effective points and therefore the predicted order of the relative prominence and frequency of occurrence of crystal faces. The Bravais rule could be considered as proposing that the order of morphological importance of the forms of a crystal would follow their interplanar spacings with cancellations exactly parallel to the lattice extinctions of X-ray diffraction theory. The Donnay-Harker Law would extend the cancellations to include the space-group extinctions as well. In this paper<sup>1)</sup> I propose first to replace the net reticular density of Bravais as modified by Donnay and Harker, by the electron density, and second to replace the concept of the order of morphological importance by the probability distribution in geological time and space. The proposed rule is that *the equilibrium crystal form is a function of the electron density and the electron density is the Fourier transform of the morphological probability distribution.*

The relative prominence of the faces of a mineral species should be determined by the specific surface energies (Gibbs, 1878, Curie, 1885, cited in v. LAUE [3] and WULFF [4], cf. especially HARTMANN and PERDOK [5]). Since the forms present on a crystal reflect the environment of crystallization as well as internal factors, Niggli's statistical measures of morphological data are ordinarily used (DONNAY and HARKER [6]) with the assumption that external effects will cancel out. Niggli's  $P$  or *Persistenz* value was used by HARTMANN and PERDOK [7] as the measure of specific surface energies. NIGGLI [8] defines  $P'$  for a given form as the relative frequency of occurrence in each distinct observed combination of forms (*Tracht*) in each distinct general habit (*Habitus*). It is assumed that Niggli's  $P'$  values approach the equilibrium crystal morphology as the sample space approaches geological time and space. Then

$$\sigma_i = -C_0 \ln P'. \quad (2)$$

According to LANDE [9] the weighted reciprocal lattice is empirical; the direct structure is inferential. The distribution of the atoms of the unit cell can not be deduced directly from the data of diffraction. It is obtained by a Fourier transform of the weighted reciprocal lattice *after* crystal chemical insights or image-seeking or statistical procedures have succeeded in fixing the phases of a sufficient number of Fourier coefficients. As every mineralogist knows, the axial ratios (the unscaled unit cell) and therefore the proportionate reciprocal lattice and symmetry may be derived from morphological measurements. The points of the reciprocal lattice weighted with the  $P'$  values comprise what I have designated the 'morphological intensity space'. The order ( $n$ ) of the points of the lattice so weighted ( $nh, nk, nl$ ) is taken as the first order not cancelled by the lattice and space group extinction rules. *A posteriori* specific

<sup>1)</sup> Presented in part at the 1966 meetings of the I.M.A., Cambridge, England.

surface energies,  $\sigma_i$  are calculated from the  $P'_i$  divided by the appropriate multiplicity factors  $m_i$ . By combining (1) and (2);

$$\sigma_i = -C' \ln [P'_i/m_i]/d_i \cdot 2. \quad (3)$$

These  $\sigma_i$  (or  $\sigma_{hkl}$ ) are compared with calculated X-ray structure factors,  $F_{hkl}$ , and the sum of the differences divided by the sum of the  $\sigma_{hkl}$  is the residual. The  $\sigma_{hkl}$  compared with the structure factors for Niggli's  $P'$  arrays for anglesite, barite and celestite; isostructural  $\text{PbSO}_4$ ,  $\text{BaSO}_4$  and  $\text{SrSO}_4$  respectively, (Pnma), yield uncorrected residuals of .205, .274 and .360. The same calculation using the X-ray powder diffraction data of the N.B.S. [10] standard for anglesite yields a residual of .107. Residuals of .5 or less are regarded as significant in X-ray diffraction analysis (BUERGER [11]). The comparison of specific surface energies with structure factors is based on the proof in MOTT and JONES [12] that the structure factors may be used to calculate the potential energy to be associated with each point of the reciprocal lattice.

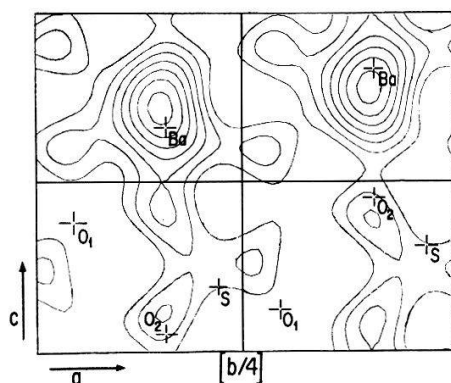


Figure 1

Fourier transform (electron density map) of the  $\gamma(1/4)$  plane of barite,  $\text{BaSO}_4$ , from the observed morphological frequencies of the fourteen most common forms ( $P'$ ). All computations and graphs by computer. Known locations of the atoms in the plane are marked for comparison. The signs of the Fourier coefficients are determined a priori by the known atomic positions.

The Fourier transform requires the observed  $F_{hkl}$  as coefficients of the terms of the Fourier series, and at least an approximation of the structure to fix the phases of each term. In the transform from the morphological intensity space, only a limited number of  $P'_{hkl}$  values (fourteen) are available from which to calculate the  $\sigma_{hkl}$ 's and only a single order for each rational direction of the reciprocal lattice. The weights of all other terms are 0. Within these severe restrictions, transforms calculated with the Niggli  $\sigma_{hkl}$  arrays yield crude electron density maps with the heavy metal peaks clearly defined (Fig. 1). Complex Patterson maps (Harker sections) have been calculated but have not yet been analysed. Structural information is required for the phases of the Fourier maps, but not for the Harker maps.

This analysis is not intended to supplant diffraction techniques but to illuminate the basic problem of the crystal polyhedral envelope. Residuals calculated using only the metal and the sulphur and neglecting the oxygens, are not substantially worse than those using the complete structure, which suggests that the equilibrium form is

principally determined by the cations. The effects of interstitial substitution and diadochy on the equilibrium form should be calculable. The absolute polarity of acentric crystals should be revealed by the Fourier map (suggested by J. D. H. Donnay). The fact that the approximate structure must be known for the Fourier synthesis (as it must for diffraction studies as well) does not invalidate the contention that the electron density is the transform of the morphological intensity space. The reasoning underlying the derivation of the  $\sigma_{hkl}$  from the  $P'_{hkl}$  may be in error, in which case, other reasoning will account for the observed agreement with calculated  $F_{hkl}$ 's. Fundamentally, if Lande's assumption of the reality of the reciprocal lattice is

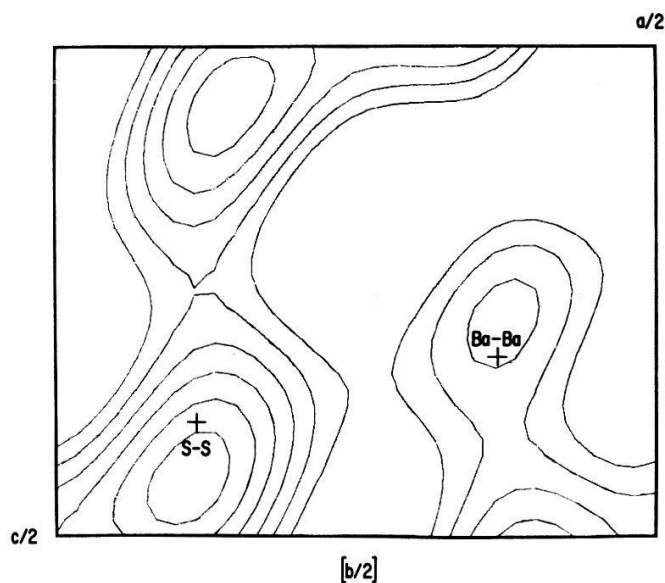


Figure 2

Fourier transform (Patterson-Harker map) of the  $y(1/2)$  plane of barite using the same  $\sigma_{hkl}$  values for coefficients as in Figure 1 but squared (without a priori phase information). The Ba-Ba and S-S positions for the inversion peaks calculated from the known parameters, are marked for comparison.

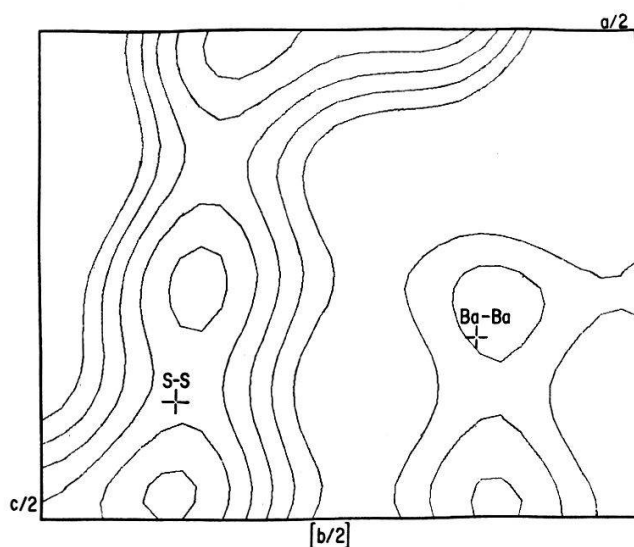


Figure 3

Fourier transform (Patterson-Harker map) as in Figure 2 but computed from the known parameters; coefficients are the squares of the calculated X-ray structure factors.

granted, then the mathematical transformations effective in diffraction analysis must apply regardless of the original source of the intensity space, whether X-ray or electron diffraction, or morphological analysis.

Many of these ideas took form during 1961–62 when with the kind encouragement of Dr. BUSCH, I visited the Festkörper Institute of the ETH. The National Science Foundation and the Graduate School of the University of New Hampshire have supported these efforts.

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## Zur Systematik der Kristallstrukturen einiger B-B-Phasen

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(26. II. 68)

*Zusammenfassung.* Es wird ein Modell für den Einfluss der Rumpfelektronen besonders von schweren Atomen auf die Kristallstruktur von B-B-Phasen angegeben. Das Modell wird angewandt auf einige Strukturen von einkomponentigen und zweikomponentigen Phasen aus B-Elementen. Es gestattet einige seither unverstandene Erscheinungen auf Eigenschaften der Bindungsbeziehung zurückzuführen. Die Überlegungen sind auch für andere Legierungsarten von Bedeutung.

### Einleitung

Die heutigen Untersuchungen zur Frage nach dem atomaren Aufbau der Festkörperphasen und nach den Gründen für das Auftreten eines bestimmten Strukturtyps werden später einmünden in eine rationelle Bindungslehre der Kristalle. Vorerst ist jedoch der Aufbau einer rationellen Systematik der Kristallstrukturen notwendig. Hilfsmittel zur Gewinnung einer Systematik sind Modelle, die der physikalischen Situation einen gewissen Ausdruck verleihen. Diese Modelle müssen heuristisch begründet werden, weil noch keine rationelle Bindungslehre vorhanden ist. Bei der