

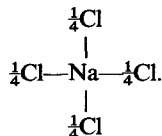
## Cleavage energies of minerals

THE phenomenon of cleavage has been used diagnostically by mineralogists throughout the history of their science, and it was one of the triumphs of X-ray crystallographers that the crystal structures which they started to reveal from 1914 onwards provided qualitative explanations of the known cleavage properties. Cleavage planes could be identified with those planes across which chemical bonding could be seen to be minimal. In extreme cases, as in graphite or talc, the distinction is absolute: bonding across the cleavage plane is confined to van der Waals forces whereas in other directions strong covalent or ionic bonding is involved. In the majority of cases the distinction is less clear cut, but if the bonding is essentially covalent throughout it is easy to count the bonds per unit area crossing any given plane; thus for example in diamond the numbers of bonds crossing unit areas of the (100), (110), (010), and (111) planes are in the ratios 4:2.83:3.58:2.31 which is consistent with the (111) cleavage.

However, in ionically bonded structures the situation is more equivocal. Although structure models depict bonds between the cations and anions these do not represent the whole story. Electrostatic attractions between oppositely charged second nearest neighbours may represent an important fraction of the bonding in any given direction, and repulsions between ions of like charge must also be taken into account. A solution to the problem is therefore most appropriately found through calculations of partial Madelung energies. The crystal structure is divided up into slices bounded by the set of planes on which the cleavage energy is to be assessed; the Madelung constant for the two-dimensional crystal slice is then evaluated and the fractional difference of this from the

Madelung constant of the whole crystal then represents the fraction of the cohesive energy that must be expended in cleaving the slice out of the crystal. One half of this then represents the cleavage energy for the plane in question.

In the direct computation of Madelung energies by calculating the electrostatic attraction between the contents of unit cells it is convenient to use the concept of Evjen cells (Evjen, 1931) in which the cells are rendered non-polar by attributing appropriate fractional charges to those ions that occur on the faces of the cell. In the present work it has been found conceptually useful to extend this idea so as to define an ionic crystal as made up of 'Evjen molecules' that are neutral and non-polar. Such Evjen molecules are arbitrary entities that may be chosen in infinitely many ways: the most suitable choice depends on the particular plane whose cleavage energy is to be evaluated. For example, in considering the (100) plane of halite it is convenient to use a square planar Evjen molecule



Such molecules fit together (with overlap of four  $\frac{1}{4}\text{Cl}$  units at each Cl site) to give a complete slice of the halite structure that is neutral and non-polar. Its Madelung constant may be simply computed from the self-energy of the Evjen molecule in terms of the Na-Cl distance ( $d$ )

$$-4 \frac{1}{4} \cdot \frac{1}{d} + 4 \frac{1}{4^2} \cdot \frac{1}{d\sqrt{2}} + 2 \frac{1}{4^2} \cdot \frac{1}{2d}$$

together with a summation of appropriate potential energy terms due to rings of surrounding Evjen molecules out to a sufficient distance (a small number times the unit cell dimension) to obtain a satisfactory degree of convergence. In principle this is the only computation needed, but in practice it is desirable also to compute the energy terms due to the arrays of Evjen molecules in a small number of parallel slices to check that the known value of the Madelung constant of the crystal is adequately approximated. This provides a check on the correctness of the programme and that a sufficient number of terms have been included to give convergence.

A difficulty arises when the plane whose cleavage energy is to be evaluated divides the structure into two parts that would have net charges. This occurs

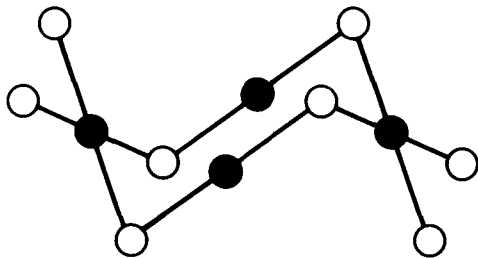


FIG. 1. The Evjen molecule used for evaluating cleavage on (111) of halite: full circles  $\frac{1}{2}\text{Na}$ , open circles  $\frac{1}{4}\text{Cl}$ . Plane of Na ions parallel to (111).

for the (111) plane of halite and for the (100) plane of fluorite in the cases considered so far, and it is physically unrealistic. If a crystal did fracture in such a direction there would have to be sufficient departures from a perfectly flat plane to permit local neutralization of charge. There are also mathematical difficulties involved. Thus the obvious Evjen molecule to use for the (100) plane of fluorite is a square pyramidal  $\text{Ca}(\frac{1}{2}\text{F})_4$  with its base on the (100) plane, but such a molecule would possess a dipole and a summation of potential energy terms due to an array of such molecules would not converge to the Madelung value. An attractive device to avoid the problem would seem at first sight to divide the crystal into non-polar Evjen slices which share partial ions with one another. This would be achieved by using cubic  $\text{Ca}(\frac{1}{4}\text{F})_8$  molecules to evaluate the (100) plane of fluorite but this procedure still leads to an excessively high cleavage energy for the plane of 15% of the Madelung energy of the crystal. This is because the Madelung energy of such a slice is diminished (numerically) by the repulsions between the large number of close contacts of partial anions. It was concluded that the minimum cleavage energy would be obtained if there were no sharing of partial ions between adjacent slices, but that the charge neutralization were as local as possible. For fluorite (100) this was achieved by using tetrahedral  $\text{Ca}(\frac{1}{2}\text{F})_4$  molecules corresponding to omission of alternate vertices of the  $\text{Ca}(\frac{1}{4}\text{F})_8$  cubes. In the case of halite (111) the problem proved more difficult and was only resolved by using the dimeric unit  $(\frac{1}{2}\text{Na})_4(\frac{1}{4}\text{Cl})_8$  shown in the figure. It is clear that each case must be treated on its merits.

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The results obtained are as follows, with the cleavage energies expressed (a) as percentages of the total Madelung energy of the crystal, and (b) in energy per unit area relative to that for the cleavage plane itself. In each case an indication is given of the form of the Evjen molecule that was used.

		(a) (%)	(b)
Halite	(100) square planar $\text{Na}(\frac{1}{4}\text{Cl})_4$	3.9	1
	(110) linear $\text{Na}(\frac{1}{2}\text{Cl})_2$	12	2.2
	(111) $(\frac{1}{2}\text{Na})_4(\frac{1}{4}\text{Cl})_8$ , see fig. 1	11	3.3
Fluorite	(100) tetrahedral $\text{Ca}(\frac{1}{2}\text{F})_4$	8	2.4
	(110) flat rectangular $\text{Ca}(\frac{1}{2}\text{F})_4$ parallel to (110)	8	1.7
	(210) flat rectangular $\text{Ca}(\frac{1}{2}\text{F})_4$ parallel to (110)	21	5.6
	(111) oblate trigonal antiprism $\text{Ca}(\frac{1}{3}\text{F})_6$	2.9	1

Although the perfect cleavage of fluorite on (111) is well known, it is interesting that 'an indistinct parting or cleavage' on (110) is also said to occur (Palache *et al.* 1951) and the calculated relative cleavage energy per unit area accords with this observation.

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## A Carboniferous arfvedsonite-aegirine trachyte from West Kilbride, Scotland

WEST of Glasgow in the West Kilbride-Fairlie district of Strathclyde Region the sedimentary rocks underlying the Clyde Plateau Carboniferous lavas are intruded by a number of sills of trachyte and felsite. The rocks forming these sills are highly altered, their ferro-magnesian minerals being usually completely decomposed so that their exact original nature has been unknown. Brief mention of these rocks has been made by Geikie (1903, p. 64) and

by Wilson in Richey *et al.* (1930, p. 87). Material containing some unaltered amphibole and clinopyroxene has recently been discovered and is described here. The specimens came from the now disused Biglees Quarry which is 500 m SSE of Biglees Farm and 3.5 km north of West Kilbride; the grid reference of the quarry is NS 210 516. The quarry rock is a rudely columnar trachyte containing small feldspar phenocrysts. The intrusion is a