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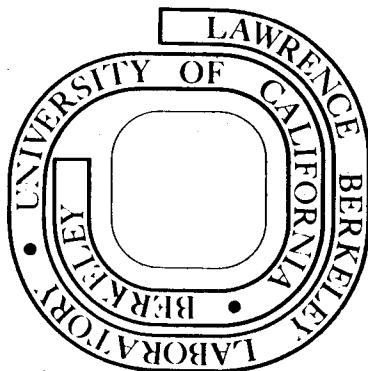
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SURFACE ENERGY OF SPINEL

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ABSTRACT

The contributions of the Coulomb electrostatic interaction and the Born-Mayer repulsive interaction to the surface energy of MgAl_2O_4 are calculated. These results are compared with the surface energy values calculated from elastic constants. The results show that surfaces parallel to $\{111\}$ planes are of lowest energy for MgAl_2O_4 spinel as well as some spinel ferrites. Except for qualitative evidence, most of these predictions await experimental verification, including the predictions of the composition of freshly cleaved spinel surfaces.

I. INTRODUCTION

Surface energy, defined as the excess energy of a free surface compared to that of the bulk, is an important parameter of a ceramic material. It controls many chemical and physical processes⁽¹⁾ such as sintering, mass loss, adhesion, crack nucleation and growth, colloid dispersion, diffusion bonding etc. A precise knowledge of this quantity would be very useful in estimating and optimising processing and properties of ceramic materials. Unfortunately, for most materials, due to various theoretical and experimental difficulties as reviewed by Rhee⁽²⁾, a precise value for this parameter is not easily obtained. While it has been measured for a very limited number of materials, theoretical calculations have been restricted to solids with simple structures⁽³⁾, for which good agreement with experimental values have been found (e.g. Ref. 4). Extension of the calculations to complex ionic solids has been lacking due to insufficient knowledge about the repulsive potential functions, although such calculations may be of practical interest since a number of complex technological materials are ionic in nature, e.g. ferrites, titanates, etc.

The repulsive interaction parameters can be determined⁽⁵⁾ from the lattice parameter and compressibility data in the case of simple rock-salt structure compounds. However, the same is not true for more complex compounds where the nearest neighbors may not always be the same. The spinel structure⁽⁶⁾ is a good example in which the octahedral and tetrahedral sites in the face centered cubic packing of anions are partially filled with cations. MgAl_2O_4 , spinel ferrites and thiospinels

possess this structure. Recently, it has been possible to estimate⁽⁷⁾ the Born-Mayer repulsive interaction parameters of MgAl_2O_4 from its infrared and Raman spectra. Thus, it is now possible to estimate the surface energy using the Coulomb and Born-Mayer potentials. The present paper describes the method and results of calculations of the surface energy of MgAl_2O_4 spinel. Also, for comparison, the values of surface energy of MgAl_2O_4 and some other spinel ferrites have been estimated from the elastic constants following a method outlined by Gilman⁽⁴⁾. Some qualitative experimental evidence in support of the results is presented, and other predictions are discussed.

II. ATOMISTIC CALCULATION OF SURFACE ENERGY

A. Method of calculation:

For an ionic solid, the surface energy, ν , can be written as a sum of two parts:

$$\nu = \nu_0 + \Delta\nu \quad (1)$$

ν_0 is the energy of the surface when the ions are held rigidly everywhere just as the ions in the bulk, and $\Delta\nu$ is a small correction that takes into account relaxation of the surface. Consider a semi-infinite crystal bound by a planar surface and choose two of the fundamental translation vectors $\vec{a}$ and $\vec{b}$ in a plane parallel to the surface with the third fundamental translation vector $\vec{c}$ normal to it outwardly. In the rigid lattice approximation, ν_0 of the surface defined by the vectors $\vec{a}$ and $\vec{b}$ is the negative of the interaction energy of the crystal⁽⁸⁾ with a stack of lattice cells along the $\vec{c}$ axis divided by twice the contact area $|\vec{a} \times \vec{b}|$. The atomic re-arrangement and the electronic polarisation tend to minimise this energy, and hence $\Delta\nu$ is a negative quantity.⁽⁹⁾ Its estimation requires a knowledge of the equilibrium surface structure which is not known for spinels. To a first approximation, $\Delta\nu$ is neglected in the present calculation, and thus the results here pertain to an ideal undistorted surface.

Assuming additive central forces, the interaction potential between the i th and j th ions is given by⁽¹⁰⁾

$$V(R_{ij}) = Z_i Z_j \frac{e^2}{R_{ij}} + b_{ij} e^{-\left(\frac{R_{ij}}{r_0}\right)} - \left(\frac{c_{ij}}{R_{ij}^6} + \frac{d_{ij}}{R_{ij}^8} \right) \quad (2)$$

In Equation (2), the first term on the right is the Coulomb electrostatic contribution, the second term is the Born-Mayer repulsion contribution

and the third term in the bracket is the Van der Waals interaction contribution for the hard-shell repulsion model. No estimate of the constants c_{ij} and d_{ij} appearing in the third term in Eqn. (2) can be made at this time for spinels and hence only the first two terms are considered below. In all these approximations, the present work compares with that of Born and Stern⁽¹¹⁾ for NaCl where both the relaxation and Van der Waals interactions were neglected.

(i) Contribution from Coulomb Interactions:

In order to calculate the surface energy as defined earlier, one needs to calculate first the interaction energy between two parallel planes P and P' in Fig. 1. Following the method of Lennard-Jones and Dent⁽¹²⁾ (so that the energy is expressed as a sum in the real space), let ions of charges q and q' be placed in a two dimensional periodic array with identical periodicities on planes P and P' respectively in Fig. 1. With Ω as the origin, and O and O' as the position of an ion on P and its projection on P' respectively such that $OO' = \vec{z}$, and $O'\Omega = \vec{r}$; the position of an ion on P' with respect to the ion at O is given by $\vec{R}_i = \vec{z} + \vec{r} + \vec{\rho}_i$, where $\vec{\rho}_i$ is the two dimensional vector joining any ion to Ω on P'. If the interaction energy between the ions is denoted by $W(R_i)$, then the energy of the charge at O due to the charges on P' is given by

$$\chi(z) = \sum_i W(|\vec{R}_i|) = \sum_i W(|\vec{z} + \vec{r} + \vec{\rho}_i|) \quad (3)$$

$$= \sum_i \int e^{ikz} e^{i\vec{k}_\perp \cdot (\vec{\rho}_i + \vec{r})} \omega(\sqrt{k^2 + k_\perp^2}) dk d^2 k_\perp \quad (4)$$

$\omega(K)$ is the Fourier transform of $W(R_i)$ and $K^2 = k^2 + k_\perp^2$; k being the component of $\vec{K}$ parallel to $\vec{z}$ and $\vec{k}_\perp$, parallel to the plane P'. In terms of the two dimensional reciprocal lattice vector $\vec{g}$, and unit cell area S

$$\sum_i e^{i\vec{k}_\perp \cdot \vec{\rho}_i} = \frac{(2\pi)^2}{S} \sum_{\vec{g}} \delta(\vec{k}_\perp - \vec{g}) \quad (5)$$

Thus,
$$\chi(z) = \frac{4\pi^2}{S} \sum_{\vec{g}} \int e^{ikz} \omega(\sqrt{k^2 + g^2}) e^{i\vec{g} \cdot \vec{r}} dk \quad (6)$$

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For the Coulomb interaction, $\omega(K) = \frac{qq'}{2\pi^2 K^2}$, the interaction energy per unit area between the planes P and P' is given by

$$\begin{aligned}\phi(z) &= \frac{\chi(z)}{S} = \frac{2\pi qq'}{S^2} \sum_{\vec{g}(|\vec{g}| \neq 0)} e^{i\vec{g} \cdot \vec{r}} \frac{e^{-gz}}{g} \\ &= \frac{4\pi qq'}{S^2} \sum_{|\vec{g}| > 0} \frac{e^{-gz}}{g} \cos(\vec{g} \cdot \vec{r})\end{aligned}\quad (7)$$

In the above equation, $|\vec{g}| = g$ and is the magnitude of $\vec{g}$. By including more atomic planes on either side of P and P' in calculating $\phi(z)$, the interaction energy between the two halves of the crystal can then be estimated. Calculation of the interaction energy between planes on only one side of P or P' is unnecessary since these planes retain the bulk environment even after the surface has been created between P and P'.

(ii) Contributions From the Born-Mayer Interaction:

Since the Born-Mayer interaction is very short range in nature, any significant contribution comes from the nearest neighbour repulsion only. Eqn.(6) with appropriate $\omega(k)$ can be used to calculate this contribution. However, it turns out that, in a complex structure where more than one b and r_0 are involved, it is simpler to first calculate the energy for different individual pairs of ions. The net contribution per unit area can be calculated by adding the contributions from all nearest neighbours that have ions on the opposite sides of the surface.

B) Calculations for $MgAl_2O_4$ Spinel

Single crystals of $MgAl_2O_4$ grown from the melt usually crystallize as octahedra with faces parallel to $\{111\}$ planes. (13) For a given volume V , the total surface area of a sphere is about $4.836V^{2/3}$ compared to the total surface area of $5.72 V^{2/3}$ for an octahedron and $7.21 V^{2/3}$ for a tetrahedron. Since the shape of the crystal would be such that the total energy of the surfaces $\sum_i v_i A_i$ is minimized, it can be concluded that $\{111\}$ surfaces have lowest surface energy. This is further supported by the observation of $\{111\}$ planes as the cleavage surfaces. (14) The calculations below are performed for the $\{111\}$ surfaces so that the values can be experimentally verified.

$MgAl_2O_4$ is a normal spinel with Mg ions in the tetrahedral positions and Al ions in the octahedral positions with respect to the close packed cubic packing of oxygen ions. (6) However, in order to calculate the energies of the $\{111\}$ surfaces, it is appropriate to

examine the structure of the $\{111\}$ planes. The planar atomic arrangements for an ideal spinel structure has been discussed in detail by Hornstra.⁽¹⁵⁾ Along $\langle 111 \rangle$ directions, the spinel can be considered as consisting of a 24 layer stacking of cations and anions with an interlayer spacing of $a_0\sqrt{3}/24$. The cations are distributed in "kagomé" and "mixed" layers alternately between the close packed anion layers. Fig. 2 shows the stacking sequence along with the ionic positions on $\{111\}$ planes in Hornstra's extended --ABC-- notation for AB_2O_4 spinel.

(i) Calculation of the Coulomb Interaction

Eqn. (7) is derived on the assumption that the periodicities on P and P' are the same. Since the atomic density on all the layers along <111> is not the same, ⁽¹⁵⁾ let us choose the basic two dimensional unit cell as the one corresponding to the periodicity of the charge distribution on the least populated layer - any plane from the mixed layer. The ionic configuration on the "kagomé" (or oxygen) layer can be described in terms of 3 (or 4) periodic charge distributions of the same periodicity, shifted with respect to each other. In order to obtain the total contribution from the layer, Eqn. (7) has to be summed over $\vec{r}$'s of these elementary planes. Thus the contribution of the Coulomb interaction to the surface energy is given by

$$\phi_c = \frac{4\pi qq'}{s^2} \sum_z \sum_{\vec{r}} \sum_{|\vec{g}| > 0} \frac{e^{-gz}}{g} \cos(\vec{g} \cdot \vec{r}) \quad (8)$$

If one chooses the two dimensional unit cell as the parallelogram of area $(\sqrt{3}/4)a_0^2$ as shown by the dotted line in Fig. 2, then the corresponding reciprocal lattice vector is:

$$\vec{g}_{1m} = \frac{4\pi}{a_0} [(1+m)\hat{x}/\sqrt{2} + (1-m)\hat{y}/\sqrt{6}] \quad (9)$$

The components of the four $\vec{r}$'s for the oxygen ions on C_1 sites in Fig. 2 are 0,0; $\sqrt{2}/8$, $\sqrt{6}/8$; $\sqrt{2}/8$, $-\sqrt{6}/8$; $\sqrt{2}/4$, 0 respectively. Similar considerations would apply for other ions. Carrying out the calculation of ϕ_c from Eqn. 8 until a convergent value is obtained, the contribution of the Coulomb interaction to the cohesive energy between the two parts of the crystal is found to be -7463 ergs/cm^2 across the {111} planes between two planes of the mixed layer. The calculation of ϕ_c for {110} and {100} planes by the same method yields - 16530 and -13100 ergs/cm^2 respectively.

(ii) Born-Mayer Contribution:

There are two different cation-anion first nearest neighbor distances in a spinel: d_t and d_o corresponding to the tetrahedrally surrounded Mg ions and octahedrally surrounded Al ions respectively. Also there are three different types of oxygen-oxygen nearest neighbor distances d_1 , d_2 and d_3 . Following the method of Striefler and Barsch⁽⁷⁾, we take into account both of the cation-anion interactions and only one of the anion-anion repulsions corresponding to d_1 - the distance between oxygen ions located on nonparallel tetrahedron edges. For MgAl_2O_4 , $a_o = 8.08\text{\AA}$,⁽¹⁶⁾ $\delta = 0.012$ ⁽¹⁷⁾

$$\begin{aligned} \text{So } d_t &= a_o (1/8 + \delta) \sqrt{3} = 1.918 \text{\AA} \\ d_o &= a_o \{ (1/4 - \delta) + \delta^2 / (1/4 - \delta) + \dots \} = 1.928 \text{\AA} \\ d_1 &= a_o (1/4 - 2\delta) \sqrt{2} = 2.583 \text{\AA} \end{aligned}$$

The values of r_o and b can be calculated from Striefler and Barsch's⁽⁷⁾ analysis and are given in Table I along with the values of the Born-Mayer energies for the pairs.

Depending on the nature of the planes adjacent to the surface, different numbers of cation-anion and anion-anion nearest neighbors will be broken when the surface is created. The least number of such bonds are broken if the surface is created such that the two adjacent layers of cations on the mixed layer would belong to different surfaces. This involves breaking of two tetrahedral cation-oxygen pairs and three octahedral cation-oxygen pairs per every unit area of $(\sqrt{3}/4)a_o^2$, contributing 6232 ergs/cm². Similar calculations for {110} and {100} surfaces give values of 7100 ergs/cm² in each case. The surface energy values thus obtained are respectively 4715 ergs/cm² and 3000 ergs/cm² for {110} and {100} surfaces and 615.5 ergs/cm² for {111} surfaces when the surface is created inside a mixed layer.

III. PHENOMONOLOGICAL CALCULATION⁽⁴⁾ OF SURFACE ENERGY

An estimation of the surface energy can be done by estimating the amount of work necessary to separate two internal surfaces. Let the attractive stress between the surfaces be approximated by a sine function. The stress is zero when the surfaces have their normal spacing d . As the interplanar spacing increases due to an applied stress normal to these planes, the stress rises to a maximum value σ_0 and then drops to zero when the separation of the planes exceeds the range h of the attractive forces. If y denotes the increase in the spacing, the strain between the planes is y/d and for small strains, by Hooke's Law, $\sigma = E \frac{y}{d}$.

E is the elastic modulus normal to the plane under consideration. From the above considerations. $\sigma = \sigma_0 \sin \frac{\pi y}{h}$; $h > y > 0$

and for small y , $\sigma \approx \sigma_0 \frac{\pi y}{h} = \frac{E y}{d}$ $\therefore \sigma_0 = \frac{E h}{\pi d}$

$$\text{or, } \sigma = \frac{E h}{\pi d} \sin \frac{\pi y}{h} \quad (10)$$

The work done in moving the surfaces from $y = 0$ to $y = h$, where they are no longer attracted, is $W = \int_0^h \sigma dy = \frac{E h}{\pi d} \int_0^h \sin \frac{\pi y}{h} dy$

$$= \frac{2 E h^2}{\pi^2 d} \quad \text{per unit area.}$$

This energy appears as the surface energies of the two newly created surfaces. Hence the specific surface energy may be written as

$$\gamma = \frac{E h^2}{\pi^2 d} \quad (11)$$

The value of E can be calculated from the stiffness co-efficients⁽⁵⁾.

The elastic constant normal to $\{111\}$ planes is $E_{111} = \frac{1}{3} (C_{11} + 2C_{12} + 4C_{44})$

For MgAl_2O_4 ⁽¹⁸⁾, $C_{11} = 2.825 \times 10^{12}$ dynes/cm², $C_{12} = 1.549 \times 10^{12}$ dynes/cm²

and $C_{44} = 1.547 \times 10^{12}$ dynes/cm² giving $E_{111} = 4.037 \times 10^{12}$ dynes/cm².

If we choose the periodicity d as the separation between two successive stoichiometric blocks ($d_{111} = a_o / \sqrt{3}$) and h as the smallest possible inter-layer spacing ($h_{111} = a_o \sqrt{3} / 24$), then we obtain from Eqn. (11),

$\nu = 298$ ergs/cm². Similar calculations for $\{110\}$ and $\{100\}$ surfaces give $\nu = 2702$ ergs/cm² and 1446 ergs/cm² respectively. These clearly show the dependence of ν on the surface orientation, consistent with the results of atomistic calculation.

IV. DISCUSSION

In spite of the approximations involved in calculating ν by both approaches, the results are important in three different ways. First of all, the two methods give consistent values for ν , the values obtained from atomistic calculations being about twice the values obtained from phenomenological calculations. The lowest ν 's (ν_{111}) however, are a fraction of the value estimated by Bruce⁽¹⁹⁾ from the heat of vaporisation data. Secondly, the calculations clearly show that $\{111\}$ surfaces have the lowest energy, consistent with the experimental observations mentioned earlier, but in contradiction with Bruce's contention that the ν 's he obtained are for $\{100\}$ surfaces. As already discussed, the structure of spinel is very very different from that of NaCl⁽⁵⁾ and hence the analogy that $\{100\}$ surfaces in spinel should also be the lowest energy surfaces, is in our opinion, inappropriate.

In the atomistic approach, the Vander Waals interaction as well as the relaxation effects have been neglected. Both these effects will tend to minimise ν and hence, ν obtained in section II(b) is only approximate and an upper limit. It is not clear at this stage as to how one can estimate c_{ij} and d_{ij} in Eqn. (2) reliably, and thus account for the Vander Waals energy. A knowledge of the surface structure is necessary in order to account for the relaxation effect. With the presently available surface diffraction techniques, e.g. by LEED, it might be possible to determine the atomic relaxation on MgAl_2O_4 surfaces. Both calculations also suggest that the cations of the mixed layers will be present on the two surfaces when the free surfaces are formed. This awaits experimental verification and may be important for the study of epitaxy on spinel substrates.

The results obtained here for MgAl_2O_4 may not be very different from what one would expect for other spinel structure compounds. The values of ν obtained from the phenomenological calculations for LiFe_5O_8 , NiFe_2O_4 and Fe_3O_4 (elastic constants are in Ref. 20) are summarised in Table II. It is apparent that these values of ν are very close to those of MgAl_2O_4 . Calculation of ν for these materials by the atomistic model requires the Born-Mayer repulsive interaction parameters that are not known at present. Significantly, ν is lowest for the $\{111\}$ surfaces in all cases. This is verified, at least qualitatively, from Fig. 3 where the $\{111\}$ planes are exposed after etching.

A number of methods are available to measure the value of ν and each of these methods has its own short comings^(2,3). However, it is only through experimental measurements, that one can verify these calculations and determine the power of these methods. The techniques have all the features one would normally encounter in dealing with complex ionic compounds. Hence, if proven successful, they can be applied to a large number of important inorganic ceramic materials and minerals to determine the surface energy as well as the nature of the atoms on the surfaces.

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FIGURES

FIG. 1. Sketch of two parallel planes, P and P' with periodic charge distribution.

FIG. 2. Projection of the atom positions on a (111) plane of the spinel AB_2O_4 .

Fig. 3. Scanning micrograph of a (111) surface of $LiFe_5O_8$, etched in phosphoric acid at 195°C for 15 minutes. The specimen was gold coated and examined in JSM-U3 scanning electron microscope. Three other variants $(11\bar{1})$, $(\bar{1}11)$, and $(\bar{1}\bar{1}1)$ are exposed (marked by the arrows) due to preferential etching of {111} surfaces.

TABLE I

Repulsive Interaction Parameters and Born-Mayer Energy for MgAl_2O_4

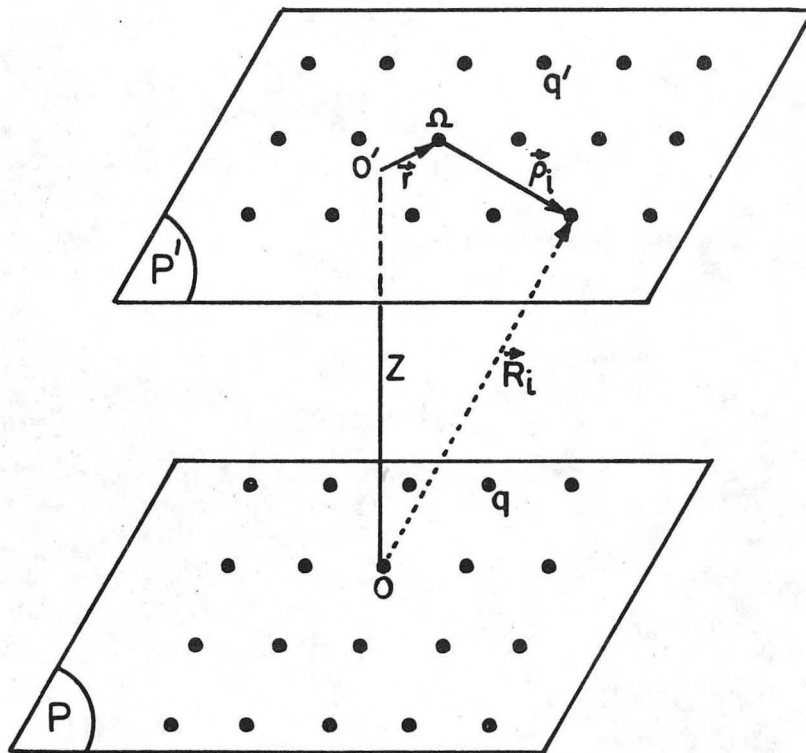
	r_0 ° (Å)	b (ergs)	$V = be^{-\frac{d}{r_0}}$ (ergs)
Mg-O	0.325	10^{-9}	2.74×10^{-12}
Al-O	0.325	1.53×10^{-9}	4.05×10^{-12}
O-O	0.275	5.95×10^{-9}	5×10^{-13}

TABLE II

Values of Surface Energies Calculated from Eqn. 11

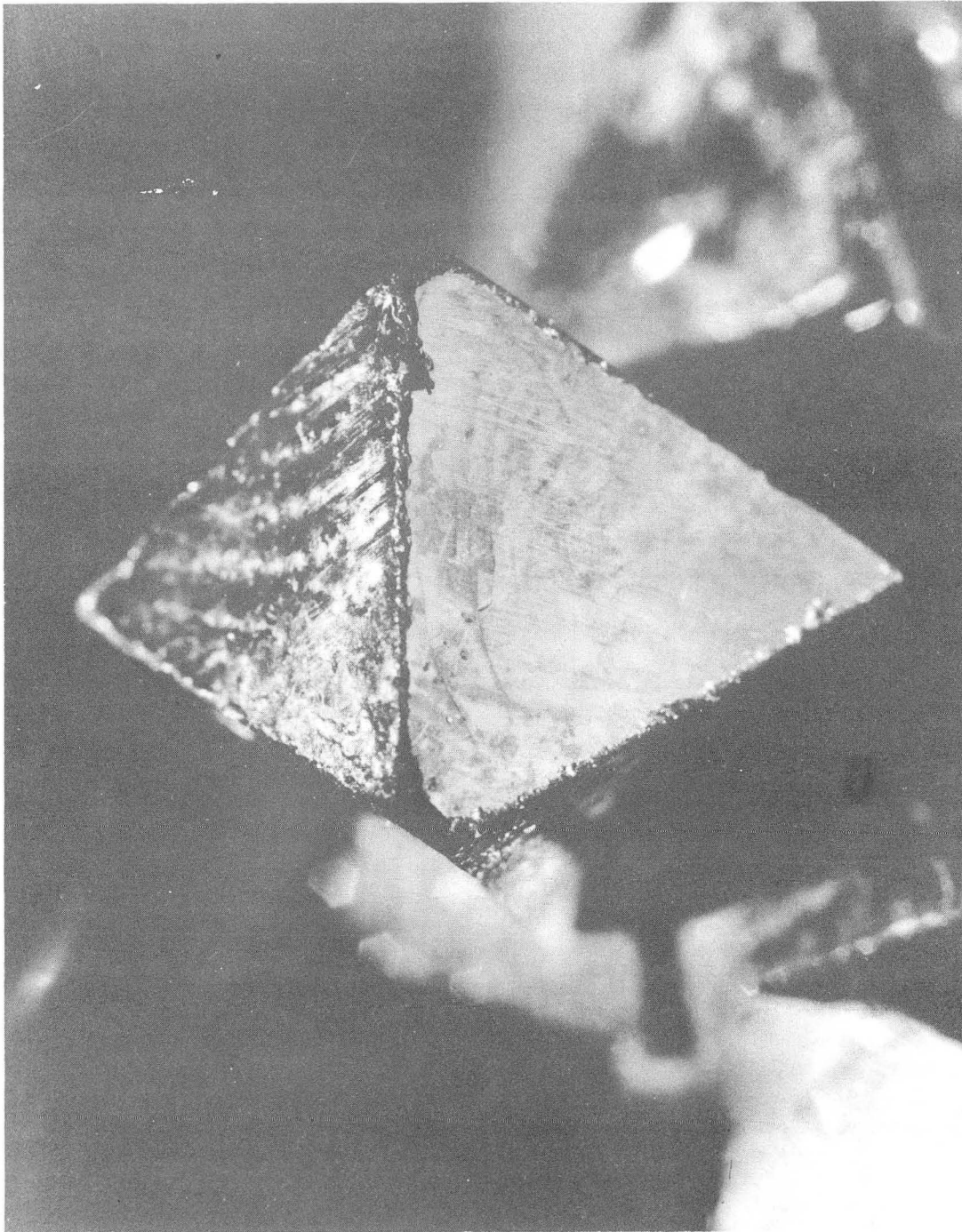
Material	{111} Surface (ergs/cm ²)	{110} Surface (ergs/cm ²)	{100} Surface (ergs/cm ²)
LiFe ₅ O ₈	222	2122	1331
NiFe ₂ O ₄	207	1837	1161
Fe ₃ O ₄	223	2164	1451
MgAl ₂ O ₄	298	2702	1446

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XBL 7510-7477

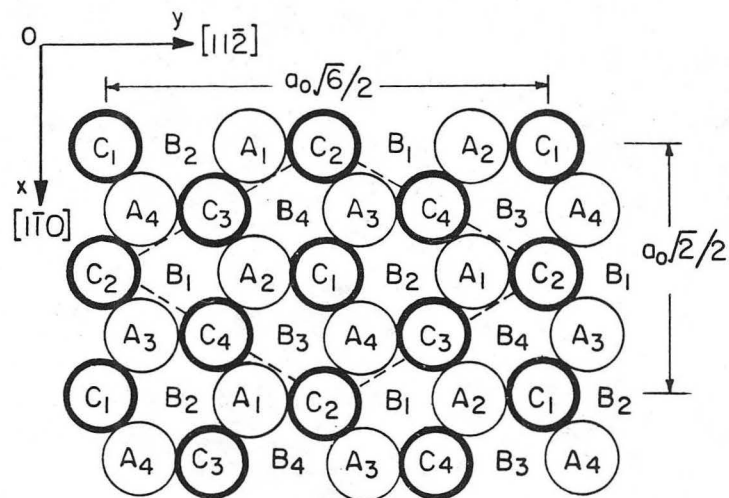
Fig. 1



XBB 764 3092

Fig. 2

Projection on (111)
 Unit Height = $a_0\sqrt{3}/24$
 Stacking in Spinel Structure
 in Extended--ABC--Notation
 Zeroth Layer (A_{1-4} Kagomé)
 at Height Zero



Occupied Positions

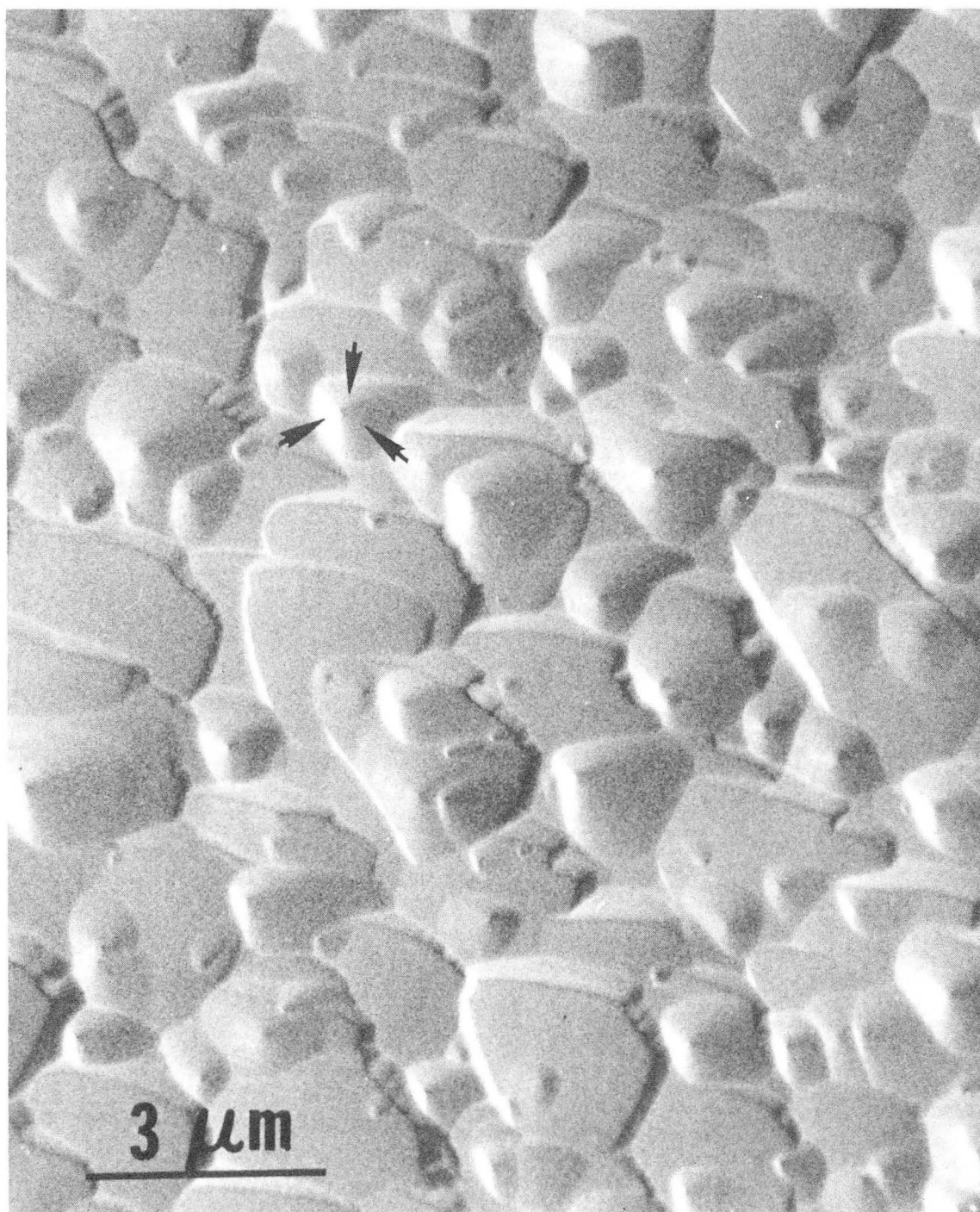
--/A₁₋₄/-/C₂₋₄/-/B₁₋₄/C₁/A₁/B₁/C₁₋₄/-/B₂₋₄/-/A₁₋₄/B₁/C₁/A₁/B₁₋₄/-/A₂₋₄/-/C₁₋₄/A₁/B₁/C₁/A₁₋₄/--

Composition in AB₂O₄

--/O₄/-/B₃/-/O₄/A/B/A/O₄/-/B₃/-/O₄/A/B/A/O₄/-/B₃/-/O₄/A/B/A/O₄--
 Kagomé Mixed

XBL 7510-7434

Fig. 3



XBB 760 10723

Fig. 4

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