

Variable Structures and Continuous Scattering of X-Rays from Layer Silicate Lattices

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Crystals of some micas and related compounds having "layer" lattices show pronounced continuous scattering of x-rays together with normal interference maxima. Continuous scattering is explained as arising from destruction of the lattice periodicity normal to the perfect cleavage of these types of substances. This is a result of translation of some layers along the b axis and parallel to the cleavage by $nb_0/3$, where b_0 is the unique lattice periodicity and n

is an integer. Various crystals differ in their degree of randomness and four general types are recognized; (1) no irregularity, (2) most elements of the crystal mosaic have a few irregular layers, (3) some elements have a regular sequence of layers while others have many irregular layers, (4) all elements have many irregular layers which leads to a small pseudo unit of structure. The phenomenon is illustrated by reproductions of photographs.

MANY crystals give x-ray interference maxima that cannot be accounted for as reflections from normal lattices. Friedrich¹ as early as 1913 observed streaks running through the normal reflections on Laue photographs of NaCl and KCl. Crystals that are naturally in a strained condition or that have been subjected to distortion show "asterism" of Laue spots which can often be removed by annealing. Barrett² considered that the anomalous reflections appearing from an iron crystal subjected to compression resulted from increased displacements of elements in the usual crystal mosaic. A similar explanation had earlier been advanced by Dickinson³ to account for anomalous reflections from potassium iodide and other alkali halide crystals. A somewhat similar explanation was given for radial streaks on Laue photographs made with the x-ray beam approximately normal to the basal cleavage of mica that had been heated or bent.⁴ These explanations treat the various "anomalous" reflections as properties of crystal aggregates.

In studying "anomalous" reflections from NaCl, MgO, and Duralumin, Preston⁵ has shown that intensities of such reflections are strongly dependent upon temperature. He, moreover, has demonstrated that they result from degradation of the crystal mosaic by lattice vibrations. The reflections are normal interference maxima from small groups of atoms having the arrangement

typical of the particular lattice. Diffuse reflections of an apparently different type have been observed to accompany age-hardening of some aluminum-copper alloys of the Duralumin class. Guinier⁶ and Preston⁷ have shown that the effects are due to segregation of copper atoms in particular lattice planes, but not in a sufficiently regular manner to give a superlattice. In one element of the crystal mosaic copper atoms tend to segregate in (010) in other elements in (100) or (001). Systematic approach to regularity among the segregating atoms can result in an asymmetric distribution of intensity in an "anomalous" reflection (Preston).

The following work deals with diffuse reflection of x-rays from several silicate minerals having "layer lattices" of which mica perhaps is the best known. Such reflections were mentioned by Mauguin⁸ and he suggested that they result from random arrangement of heavy ions in the oxygen frameworks of the structures. An understanding of the cause for the diffuse reflections leads to considerable information about the nature of the mosaic structure in these particular crystals.

EXPERIMENTAL

X-ray diffraction photographs of some mica crystals made with radiation from a tube with a copper anticathode operated at 40 kv peak and on an x-ray goniometer of the type first described by Weissenberg are reproduced in Fig. 1. An x-ray goniometer is a device in which re-

¹ Friedrich, *Physik. Zeits.* **14**, 1079 (1913).

² C. S. Barrett, *Phys. Rev.* **53**, 1021 (1938).

³ R. G. Dickinson, *Phys. Rev.* **22**, 199 (1923).

⁴ W. L. Bragg, *Nature* **124**, 125 (1929). S. B. Hendricks, *Zeits. f. Krist.* **71**, 269 (1929).

⁵ G. D. Preston, *Proc. Roy. Soc. (London)* **A172**, 116 (1939).

⁶ A. Guinier, *Comptes rendus* **206**, 1641, 1972 (1938); *Nature* **142**, 570 (1938).

⁷ G. D. Preston, *Proc. Roy. Soc. (London)* **A167**, 526 (1938); *Nature* **142**, 570 (1938); *Phil. Mag.* **26**, 855 (1938).

⁸ C. Mauguin, *Comptes rendus* **187**, 303 (1928).

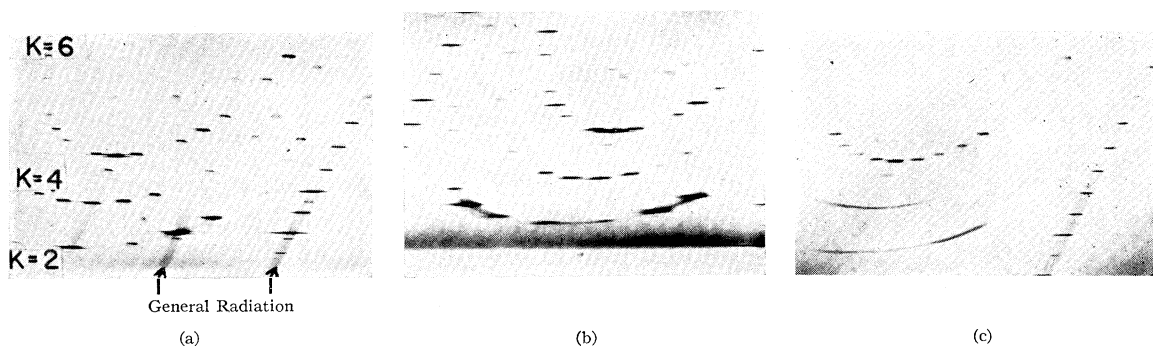


FIG. 1. X-ray goniometer photographs of three mica crystals showing various degrees of continuous scattering.

flections (spots) given by a crystal rotating about a fixed axis are recorded on a film synchronously translated behind a slit. Photographs reproduced in Figs. 1 and 3 were made on a cylindrical film coaxial with the axis of rotation of the crystal which was taken as the crystallographic a direction. They were restricted to the equatorial zone or to the first layer line by the slit before the film and thus show reflections only from planes having the h index zero, $(0kl)$, or one, $(1kl)$, respectively.

Indices of planes, reflections for which appear on Fig. 1a, are indicated on the sketch in Fig. 3d. In Fig. 1b it can perhaps be seen that curves along which k is constant show continuous scattering, particularly near some of the more intense reflections. This phenomenon which can be detected on the original of Fig. 1a is very prominent in Fig. 1c. It can further be seen from these photographs that while scattering along the $k=2$ and $k=4$ curves might either be sharp or diffuse, normal spots are present along curves having $k=0$ and $k=6$. Qualitative examination indicates that the continuous scattering has a symmetrical intensity distribution about the normal reflection in many cases.

Photographs of the first layer line of one biotite mica (United States National Museum C3675) showed pronounced continuous scattering along the $k=1$ and $k=5$ curves and very weak continuous scattering along $k=3$ curves. None was observed along $k=n \times 3$ with n odd, curves on photographs of several other micas showing pronounced continuous scattering along other k constant curves. Further experiments on crystals from one hundred different mica specimens show that continuous scattering is present, with the

one exception mentioned, only along curves having the l index variable with h and k indices constant and the k index not divisible by three, i.e., $(h_a k_a l)$, $k_a \neq n \times 3$. Eighty of the specimens were similar in structure to biotite or black mica and gave the effect with but few exceptions. None of the twenty crystals examined having the muscovite or white mica structure showed observable continuous scattering.

Curves of continuous scattering appear as

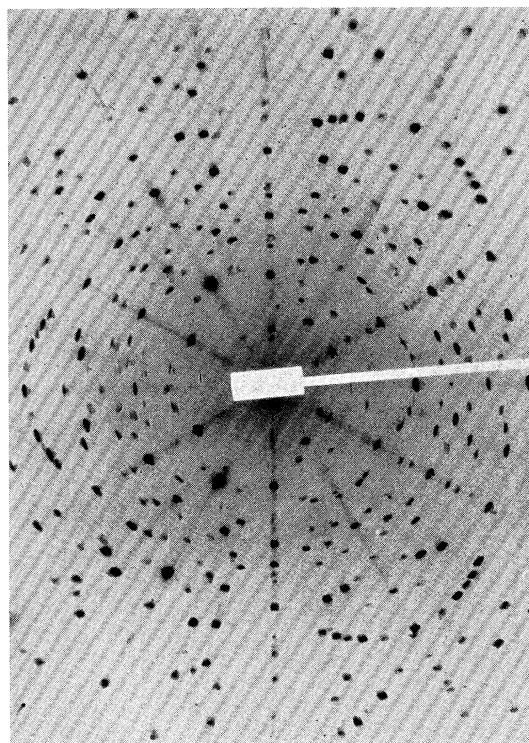


FIG. 2. Laue photograph showing radial streaks resulting from random structure.

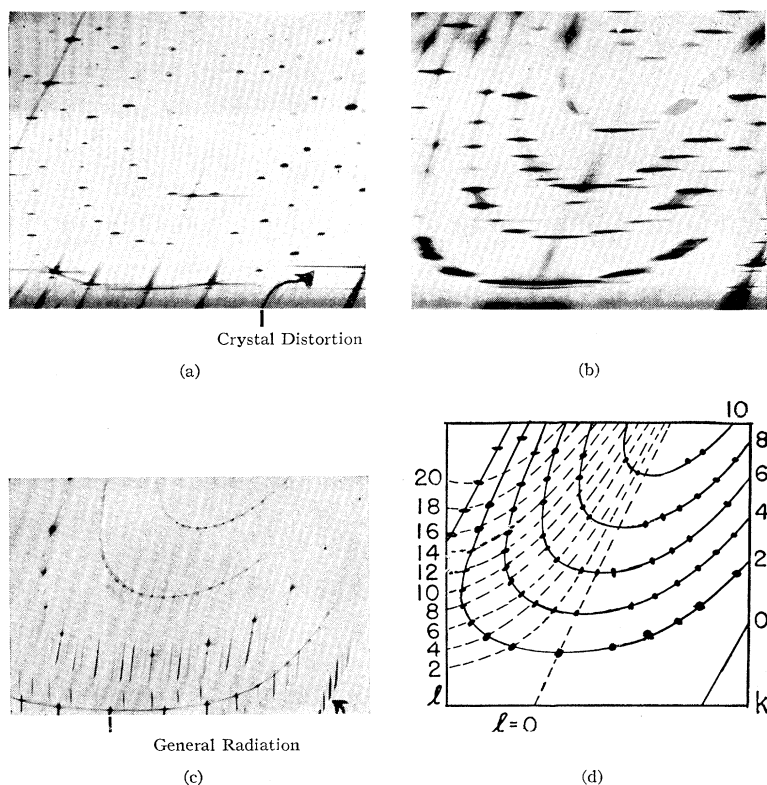


FIG. 3. X-ray goniometer photographs of (a) talc, (b) pyrophyllite, and (c) cronstedite. Indices of reflecting planes appearing on the talc photograph are indicated on the sketch in (d).

radial streaks on Laue photographs made with the x-ray beam normal to the perfect cleavage of mica, (001), and to the photographic plate. A photograph showing moderate development of streaks is reproduced in Fig. 2. Such streaks can be confused with those mentioned in the introduction as arising from crystal distortion. However, they do not show the necessary absorption limits of the photographic plate required by distortion and they are absent for some of the more intense reflections. Rotating crystal photographs from the appropriate mica specimen rotated about the a axis show continuous scattering as a continuous background along the layer lines where it cannot be confused with the trace of the general radiation. Monochromatic radiation must be used to demonstrate continuous scattering along the equatorial zone of such photographs.

Photographs made from the silicate layer minerals, pyrophyllite, talc, and cronstedite are reproduced in Fig. 3. Indices of reflecting planes for pyrophyllite and talc are shown on the accompanying sketch, Fig. 3d. The talc photo-

graph shows features similar to those generally found for biotite micas and this was true for another talc specimen. On the pyrophyllite photograph, however, continuous scattering is present not only along $k=2$ and $k=4$ curves but also, although considerably fainter, along the $k=6$ curve. Further, continuous scattering is largely restricted to regions between two normal reflections with a probable maximum value intermediate between them. Both talc and pyrophyllite crystals are very easily deformed since they are not elastic like mica. For this reason the photographs show more prominent traces due to distortion of crystals during their reduction to adequate size for use. Natural scarcity of specimens containing large crystals further limited the observations to a few samples.

The cronstedite photograph is of the first layer line with rotation about the a axis and accordingly shows reflections only from planes having k odd, $(1kl)$. It was made with radiation from an iron anticathode. Here again continuous scattering is present only along curves (h_0k_0l) , $k_0 \neq n \times 3$. Traces due to general radiation from

the source are perhaps confusing since prolonged exposures were necessary to bring out traces of continuous scattering along curves having k constant. The intensity of the continuous scattering is very weak compared with that of strong normal reflections appearing at scattering angles near 45° . Normal reflections appear along (h_0k_0l) , $k_0 \neq n \times 3$ curves but they too are very weak as compared with (h_0k_0l) , $k_0 = n \times 3$ reflections, although they are stronger than the continuous scattering. Three specimens of cronstedite were examined.

STRUCTURES OF COMPOUNDS SHOWING CONTINUOUS SCATTERING

Before advancing an explanation for the phenomenon described in the previous section, it is necessary to discuss the structures of some of the various minerals for which it has been observed; namely biotite and brittle micas, talc, pyrophyllite, vermiculites, chlorites, stilpnomelanes, and cronstedite.

Pauling⁹ showed that a number of silicates having micaceous cleavage possess the common structural element of tetrahedral SiO_4 groups, joined by the sharing of oxygen ions, at tetrahedral corners, into an extended net. These layers are combined with octahedral groupings of oxygen ions, common to SiO_4 groups, and hydroxyl ions about Fe^{+++} , Fe^{++} , Mg^{++} , Al^{+++} , Li^+ , etc. to form multiple layers. Pauling found the structures of the close knit multiple layers but he did not determine the manner in which layers are superimposed parallel to the cleavage. Later studies have been directed to this end and in them is found the explanation for the continuous scattering.

The manner in which layers are stacked is largely determined by the spatial relationship of adjacent atoms in contiguous layers. This relationship of the top of one layer to the bottom of another is fixed in every case by certain principles of structure, four different ones being involved. In brucite, $\text{Mg}(\text{OH})_2$, where hydroxyl groups are in both surfaces the superposition is determined by their close packing as spheres.

⁹ L. Pauling, Proc. Nat. Acad. Sci. **16**, 123, 578 (1930). Note W. L. Bragg, *Atomic Structure of Minerals* (Cornell Univ. Press, 1937), p. 203 f for a discussion of structures of the micas, etc., and for drawings illustrating the structures.

All the other compounds under discussion have oxygen atoms of a silicate sheet in at least one surface and micas, talc, and pyrophyllite have both surfaces of this type. In talc and pyrophyllite each oxygen ion in a surface is placed so that it has as many neighboring oxygen ions as possible in the adjacent surface which cannot be an arrangement of close packed spheres because of the oxygen positions in a surface. The superposition of silicate layers in micas is determined by the twelve-fold coordination of potassium between the layers with respect to oxygen ions in the surfaces. Vermiculites, cronstedite, and kaolin minerals have a hydroxyl group or water molecule in one layer surface so placed as to approach closely to one oxygen ion of the neighboring layer, an arrangement brought about by interaction through the hydrogen atom of the hydroxyl group.

The top layer in a sequence of biotite mica layers can have any of three orientations, differing by 60° in rotation about the layer normal, without affecting the relationship of neighboring oxygen ions in the last adjacent surface since they are arranged in an hexagonal array. Each of the three orientations, however, results in a different placing of a succeeding layer relative to the sequence and thus would produce a new lattice if repeated. Actually six different crystal structures corresponding to various regular sequences of layers have been observed among the biotite micas.¹⁰ All except one of these modifications showed continuous scattering of x-rays along the (h_0k_0l) , $k_0 \neq n \times 3$ curves.

Muscovite, the ordinary white mica, in contrast to biotite, the black mica, is invariant in structure among twenty specimens examined. The most striking difference in their diffraction patterns is the presence of $(06l)$, l odd, reflections for muscovite. This indicates that the silicate layer in muscovite is distorted from the ideal structure described by Pauling. The distortion could be a result of incomplete filling of positions with octohedral coordination, only two-thirds of which are filled with aluminum ions, accompanied by substitution of Al^{+++} for Si^{+4} in tetrahedral coordination. Irrespective of the explanation the silicate layer seems to be suffi-

¹⁰ S. B. Hendricks, Nature **143**, 800 (1939). Am. Mineral **24**, 729 (1939).

ciently distorted to make different orientations nonequivalent and thus lead to a unique structure. This might appear contrary to first expectations, but it is equivalent to stating that regular blocks (biotites) can be stacked in many more ways to fill space than can irregular ones (muscovite). Muscovite crystals, it will be recalled, show no observable continuous scattering under experimental conditions giving very pronounced effects with biotite.

Adjacent surfaces of layers in talc and pyrophyllite can have either of two relationships,¹¹ both of these further can possibly have the various orientations mentioned for biotite. Silicate layers in pyrophyllite more closely resemble those of muscovite than those of biotite micas, in that only a part of the octahedral coordination positions are filled. Pyrophyllite, however, as well as talc shows continuous scattering along the constant k curves.

Successions of kaolin layers too are determined by their orientations. Polymorphic modifications of kaolin, namely the minerals kaolinite, dickite, and nacrite, are analogous in structure to various forms of biotite mica.¹² Only dickite and nacrite form crystals sufficiently large for use on an x-ray goniometer and those of dickite are very small. Continuous scattering was not observed for either mineral. Silicate layers in the mineral cronstedite are similar to those of kaolin. In them, however, half of the Si^{+4} ions having tetrahedral coordination are replaced by Fe^{+++} ions and positions having octahedral coordination are filled by Fe^{+++} and Fe^{++} ions. Cronstedite, however, shows very pronounced continuous scattering in contrast with the other kaolin minerals; in fact it affords one of the best illustrations of the phenomenon.

EXPLANATION FOR CONTINUOUS SCATTERING. NATURE OF THE CRYSTAL MOSAIC

Since some orders of reflection from a particular plane are normal and others are diffuse, the phenomenon must be a lattice property rather than a property of a crystal aggregate. Thus in Fig. 1c the second and fourth orders of reflection from (010) are diffuse while the

more intense sixth order (060) is normal. Alternative orientations of a symmetrical layer are equivalent to translations along the b axis of the lower silicate net by $nb_0/3$ with respect to the upper. Such translations do not alter the lattice periodicities along the a axis and accordingly are without effect on the Laue conditions for interference in that direction. They determine the periodicity along the b and c axes, however, and thus determine the Laue condition in those directions. If the translations are random values of $nb_0/3$ in any crystal mosaic the c direction will have an indefinite periodicity and the reflections will be greatly broadened along the ($h_0k_0l_0$) curves. The translations are without apparent effect on the b periodicity if the k index is a multiple of three and these planes will have normal reflections with a c periodicity corresponding to one layer.

Before considering application of this explanation to the various lattices mentioned in the preceding section it is necessary to recall some features of a crystal mosaic. The concept of a mosaic crystal was introduced by Darwin in his work on diffraction of x-rays by crystals¹³ and it is not to be confused with the term as used by some later workers. Darwin demonstrated that the observed intensities of x-ray reflections require crystals to consist of many small elements of volume deviating slightly from perfect alignment. The total reflection is the summation of x-rays scattered from the various elements, which act independently of one another except for secondary extinction. While line width, line shape, and intensities are affected, the phenomenon has not been very susceptible of study and the distribution of sizes of the mosaic volumes are unknown.

If a layer in a mosaic element of a silicate mineral of the type described is translated by $b_0/3$ or $2b_0/3$ from its position in a regular lattice, the whole sequence of layers is altered and there is a resulting shift in phase of scattered radiation unless the k index is a multiple of three. The intensity of the reflection will depend upon which element or elements of the mosaic are translated. The breadth of the reflection will be a function of the number of translated elements and the intensity distribution across it

¹¹ S. B. Hendricks, Zeits. f. Krist. **A99**, 264 (1938).

¹² S. B. Hendricks, Am. Mineral. **23**, 295 (1938).
Zeits. f. Krist. **100**, 509 (1939).

¹³ C. G. Darwin, Phil. Mag. (6) **27**, 325 (1914).

will be determined by their distribution. A limiting condition will be where all approach to regularity along the c axis is destroyed. Accordingly there should be continuous scattering along the $(h_a k_a l)$, $k_a \neq n \times 3$, curves without normal reflections. In a less extreme case the continuous scattering will be restricted to the neighborhood of the normal reflections.

Analyses of the crystal structures of the micas¹⁰ show that relative intensities of normal (hkl) , $k \neq n \times 3$, reflections can be calculated by the usual methods. They decrease in absolute intensity, however, as continuous scattering increases. Some elements of the crystal mosaics therefore have regular structures while others are highly irregular after the manner described above. The number of elements in which only a few layers are translated, moreover, must be small compared with the number giving the extreme conditions. This character of the crystal mosaic of the micas is further shown by the presence of two or more different regular structures in some biotite crystals. One biotite mica sample¹⁰ had a periodicity of 240Å along the c axis, which requires regular superposition of twenty-four layers within the unit of structure. All reflections are normal and continuous scattering is not present. In order to establish the periodicity and give the observed narrow reflections the crystal mosaic must be at least ten lattice periods in thickness, 2400Å. A crystal could readily be cleaved having this thickness and in fact it should be possible to obtain one less than a lattice period in thickness. Crystals actually used were considerably larger than this, being of the order of 0.05 mm in thickness. Absence of continuous scattering in these crystals suggests that the structure is of the nature of a large regular lattice, a superlattice, and that other irregular lattices are ones having a tendency to form a superlattice from a simple array.

One modification of kaolin, nacrite, apparently has a regular lattice in most elements of the crystal mosaic since continuous scattering is not present and it is possible to calculate intensities of all reflections.¹² It too shows reflections equivalent to $(06l)$, l odd, reflections of muscovite, white mica, which indicates some distortion of the symmetrical layer that results in unique stacking of layers. In the case of dickite, a

second modification of kaolin, continuous scattering is not observed. Intensities of (hkl) , $k = n \times 3$ reflections can be calculated satisfactorily but (hkl) , $k \neq n \times 3$, intensities cannot be explained by a regular structure. It follows therefore that most of the elements in the crystal mosaic have one or several layers displaced from the regular sequence. Reflections from $(06l)$, l odd, are absent for dickite.

The mineral cronstedite affords an extreme example in that it shows practically continuous scattering along the $(h_a k_a l)$, $k_a \neq n \times 3$ curves. Intensities of (hkl) , $k = n \times 3$, reflections can be satisfactorily calculated on the basis of a pseudo-rhombohedral unit of structure formed by averaging the three orientations with equal weight.¹⁴ This pseudo-unit apparently contains fractional atoms, its contents being in various equivalent sets of points, (a) $\frac{1}{3}$ Si⁺⁺⁺⁺ + $\frac{1}{3}$ Fe⁺⁺⁺, (b) 1 Fe⁺⁺, Fe⁺⁺⁺, (c) $\frac{1}{3}$ O⁻⁻⁻ + $\frac{2}{3}$ OH⁻, (d) OH⁻, (e) $\frac{1}{6}$ O⁻⁻⁻, (f) $\frac{1}{6}$ O⁻⁻⁻. It therefore follows that every element in the crystal mosaic must have a very irregular lattice.

Lattice irregularities similar to those of cronstedite have earlier been observed in the simpler compounds NiBr₂ and CdBr₂.¹⁵ In these compounds the Br⁻ ions form cubic close packed arrays. If NiBr₂ is crystallized from alcohol the nickel ions are in definite positions having octahedral coordination as required by the cadmium chloride type of structure. Formation of crystals by sudden condensation from the vapor results in a structure having random shifting of layers while preserving close packing of ions in contiguous layers, i.e., a mixing of cubic and hexagonal close packing. Since observations have been restricted to x-ray powder diffraction photographs, possible continuous scattering has not been observed. The mineral brucite, Mg(OH)₂, might be expected to behave in a similar way but it has not been subjected to detailed study.

Both pyrophyllite and talc show continuous scattering and in both cases intensities of (hkl) , $k = n \times 3$, reflections can readily be calculated while intensities of reflection from (hkl) ,

¹⁴ S. B. Hendricks, Am. Mineral. **24**, 529 (1939).

¹⁵ J. A. A. Ketelaar, Zeits. f. Krist. **88**, 26 (1934). J. M. Bijvoet and W. Nieuwenkamp, Zeits. f. Krist. **86**, 466 (1933).

$k \neq n \times 3$, cannot be explained by a regular lattice. In both cases the continuous scattering is weak. It follows therefore that most elements of the crystal mosaic have one or more translated layers and that some elements have many displaced layers. This is intermediate between dickite and cronstedite.

Pyrophyllite and one biotite mica sample differed from the other substances examined in showing some continuous scattering along $(h_a k_a l)$, $k_a = n \times 3$, curves. In both cases this was very weak compared with that observed along $(h_a k_a l)$, $k_a \neq n \times 3$ curves, on the same photographs. Continuous scattering on the pyrophyllite photographs further has a tendency to be restricted to the region between two normal reflections with a maximum of intensity midway between them. The intensity maximum is evidence of a tendency for the crystals to form a definite superlattice. No entirely satisfactory explanation has been found for the continuous scattering

along $(h_a k_a l)$, $k_a = n \times 3$, curves for pyrophyllite, but the following might possibly hold. The parameter along the b axis (y) defining the relative positions of the layers might differ slightly from $nb_0/12$. Irregular sequence of layers in an element of the crystal mosaic thus would have some effect on the (hkl) , $k = n \times 3$ reflections. An alternative explanation would be that the layers in pyrophyllite are somewhat distorted in a manner similar to that of muscovite but not sufficiently to prevent random orientations. Reflections from (hkl) , $k = n \times 3$ and l odd, would normally appear though weak for a regular structure and would be broadened to the point of not being observable as irregularity was introduced. The actual photographs might be an intermediate stage in this process. Composition of the specimen examined eliminates any possibility that the phenomenon was caused by the nonhomogeneous distribution of some component.

Excited States of the O^{16} Nucleus

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IN a recent Letter to the Editor, Oppenheimer and Schwinger¹ have discussed the excited states of the nucleus O^{16} which are formed subsequent to the bombardment of fluorine by protons. Fowler and Lauritsen² have shown that this bombardment gives rise, in addition to short and long range groups of α -particles, to monochromatic γ -rays of energy 6.3 ± 0.1 Mev and to the production of pairs with the energy of 5.9 ± 0.3 Mev. According to the interpretation of Oppenheimer and Schwinger, the pairs are produced by internal conversion from an excited state of O^{16} which has zero angular momentum and even parity to the ground state which is likewise a 0^+ state. The γ -rays, on the other hand, result from a transition from an excited

1^+ or possibly 2^- state to the ground state. It is rather essential for this explanation that there exist no intermediate excited levels of such a character that transitions to them from the upper states will be of sufficient intensity to compete actively with the pair production or with the 6.3-Mev γ -ray transitions. The object of the present note is to examine the levels of O^{16} as predicted by the α -particle model and to see to what extent they may satisfy the requirements postulated by Oppenheimer and Schwinger. It is clear that the independent particle model will not readily predict a low excited 0^+ state since the first steps of excitation will probably consist in raising a particle from a P state to a $2S$ state, thus producing levels of the type 2^- , 1^- and 0^- .

The O^{16} nucleus will be thought of as a close packed grouping of four α -particles whose equilibrium configuration is that of a regular

¹ J. R. Oppenheimer and J. S. Schwinger, Phys. Rev. **56**, 1066 (1939).

² W. A. Fowler and C. C. Lauritsen, Phys. Rev. **56**, 840 (1939).

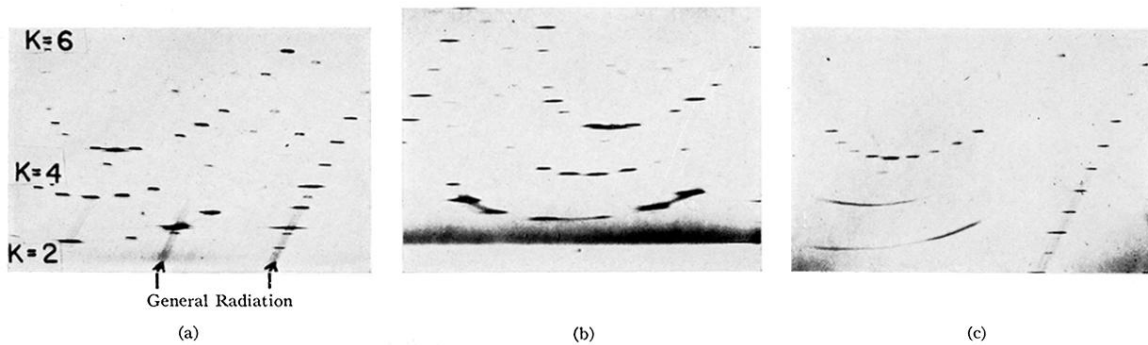


FIG. 1. X-ray goniometer photographs of three mica crystals showing various degrees of continuous scattering.

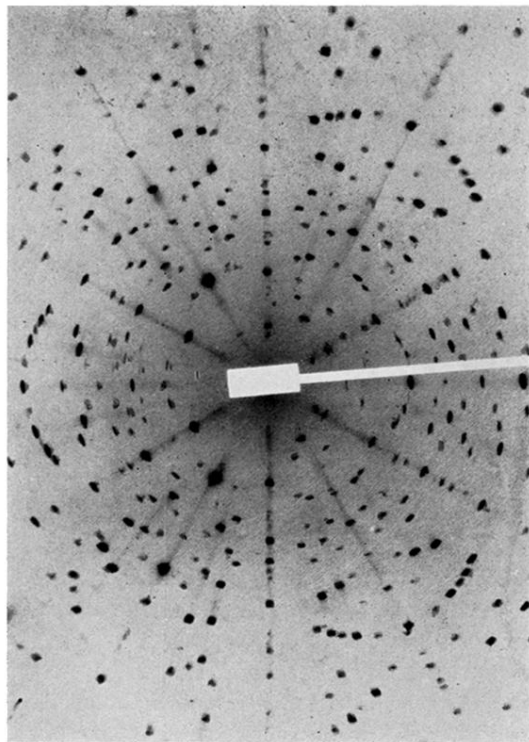
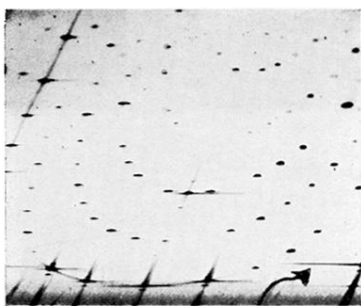


FIG. 2. Laue photograph showing radial streaks resulting from random structure.

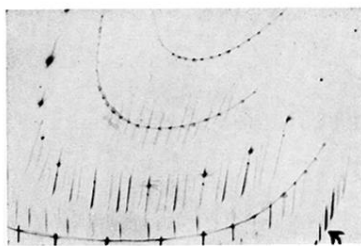


Crystal Distortion

(a)

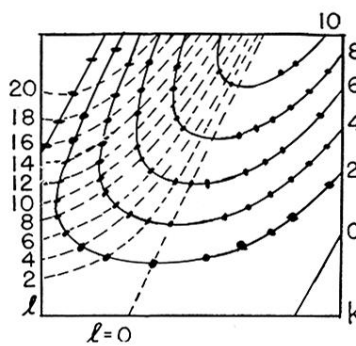


(b)



General Radiation

(c)



(d)

FIG. 3. X-ray goniometer photographs of (a) talc, (b) pyrophyllite, and (c) cronstedite. Indices of reflecting planes appearing on the talc photograph are indicated on the sketch in (d).