

## Equilibrium Diagrams and Single Crystal Growth

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The crystal grower is a specialist who operates at the second step of a chemical preparation experiment. The first step is the synthesis of the compound; it yields polycrystalline material of varying degrees of fineness. In this step the chemist has been quite successful. Among naturally occurring compounds (minerals), only a short list remains to be synthesized.

The second step of the experiment is the conversion or ordering of the polycrystalline synthetic product into a single crystal. An even higher level of operation may be superimposed on this experiment in that not only must the crystal be single (1) but it must also be chemically homogeneous and possess a high degree of perfection. As operations go in the laboratory, step 1, synthesis, is easy; step 2, single crystal growth, advances satisfactorily; but step 3, perfection, is a matter of extreme difficulty. For practical laboratory reasons, one must grow crystals under conditions that depart from equilibrium ones. It is the purpose of this discussion (2) to relate the data of equilibrium as illustrated in the phase equilibrium diagrams (3) to the possibility of single crystal growth.

Figure 1 shows an idealized binary phase equilibrium diagram with two compounds (one melting incongruently), two eutectics, and one peritectic. The liquidus line (*ABCOEG*), under equilibrium conditions, is the locus of all points of liquid-solid equilibria. Crystal growth from the melt requires operating, under conditions of supersaturation, at some temperature below this liquidus. This set

of conditions is not known but must be fixed by trial and error, usually by setting up a thermal gradient, the sharp region of which contains the liquidus isotherm. The points marked *A*, *C*, and *G* (Fig. 1) are congruent melting points of compounds. These points represent compositions ideal for crystal growth by either the crucible lowering or the withdrawal method. While one can never be certain of achieving the exact diagram composition, small deviations are apparently permissible (near 1 percent). Deviations from the true stoichiometry characteristic of the compound are also allowed.

Compositions on this diagram will be related to growth from the melt by three methods, (i) the crucible method, (ii) the withdrawal method, and (iii) the flame fusion method.

### Crucible Method

In the crucible method, a cylindrical crucible with a cone-shaped tip containing the melt is lowered through a furnace in which there is established a sharp thermal gradient. As the tip of the cone passes through that isotherm near the liquidus of the melt (some isotherm below the melting point within the region of metastable supersaturation), it is hoped that one nucleus will form to the exclusion of others and that, with further lowering, this nucleus will grow to fill the crucible with one crystal. Thus the method is an attempt to depart from normal freezing to a polycrystalline ingot by inducing nucleation in a small volume of melt.

The sharpness of the thermal gradient in the critical region of phase change and

the rate of lowering are two important physical factors for obtaining single crystals. Although these factors have been recognized, their respective contributions have not yet been analyzed (4). It is common experience that lowering the crucible too rapidly will yield an ingot with a single-crystal skin and a polycrystalline interior or pipe. The thermal gradient and the rate of lowering are the heat sink for extraction of the energy change of freezing, and this part of the operation fails if either is inadequate.

From a chemical point of view, a truly one-component system with congruent melting point (and no lower inversions) is desired. To maintain this desirable chemical composition there must be no chemical contribution from the atmosphere (oxidation-hydrolysis) or from the crucible (thus insuring a one-component system). A second solid phase, scum, or oxidation products offer undesirable and uncontrollable points of local nucleation.

So far only one-component melts have been considered. Another different composition on the diagram is the isopleth *D* (Fig. 1). A melt of this composition yields, on cooling, crystals of  $XY_n$ . Below the liquidus (*CB*), these crystals are in equilibrium with a mother liquor whose composition varies with temperature. The composition of this liquid at any temperature is given by the intersection of the isotherm with the liquidus *BC*. Final solidification takes place at *B*. On cooling, this liquid crystallizes as  $XY_n$ , and the liquid is enriched in *X*.

Some idea of the influence of impurities (solid solution) on the ease of growth of single crystals is available from the work of Goss (5). Goss added known amounts of antimony, cadmium, lead, zinc, silver, and indium to 99.997-percent tin and grew crystals from these melts. The influence of the impurities on the texture was a function of the amount of addition. For a melt where the addition was 0.1 percent of the solid solubility limit, it was not possible to obtain single crystals under conditions of rapid growth. Single crystals could be obtained at slower growth rates, but they had marked superstructure. When the level of impurity was 0.01 percent of the solid solubility limit, there was no effect on the ease of growth of single crystals, but there was a continual effect on the texture. Crystallization of  $XY_n$  from such a liquid is very significantly different

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from crystallization from its own melt in that the solid phase is in equilibrium with a liquid of constantly varying composition. It is true that the liquid is always crystallizing  $XY_n$ , but the environment in the neighborhood of the growing face of crystal  $XY_n$  is a varying one, and hence the crystal growth may become diffusion-controlled. In addition, the nucleation process is forced into a different environment. Attempts at U.S. Naval Research Laboratory to grow single crystals of such binary melts by the crucible method have been uniformly unsuccessful. The isopleth  $F$  (Fig. 1) presents the third type of melt on this diagram. This composition, on cooling to the liquidus  $EG$ , yields crystals of  $Y$ . On further cooling,  $Y$  continues to crystallize out, the liquid changing in composition along  $EG$  toward  $E$ . When the composition  $E$  is reached, an isothermal reaction occurs.  $Y + \text{liquid} = XY_m$  and for composition  $A$  final crystallization takes place, yielding a single phase  $XY_m$ . Conversely,  $XY_m$  melts incongruently to yield  $Y + \text{liquid}$ .

Such a composition as  $A$  does not lend itself to single-crystal growth by the crucible-lowering method. Successful completion of the liquid-solid reaction under the conditions of growth would be nearly impossible. The crucible method can be operated using an oriented seed in the tip with considerable difficulty of control. The orientation of the single crystal obtained by the usual spontaneous nucleation in a cone tip is a function of (i) thermal gradient, (ii) rate of lower-

ing, and (iii) the principal growth direction of the phase. The particular function is as yet unknown.

### Withdrawal Method

In the withdrawal or Kyropoulos method, one uses a stationary crucible placed in an open furnace, thereby providing a thermal gradient above the melt. A cold finger is lowered into the melt to initiate crystallization. The resultant crystal mass on the cold finger is withdrawn from the melt by an elevator. This initial mass can be made up of several crystals. In the withdrawal method, this mass from within the melt was raised until the smallest contact was made with the surface of the melt (hopefully a single-crystal contact). Then, by adjusting the gradient slightly, we allowed this contact to widen to a larger diameter and then grow. In effect, then, a portion of the initial polycrystalline mass seeded the melt. Of course, in practice, one commonly uses single-crystal seeds held in a chuck on the cold finger.

The composition limitations of the crucible and withdrawal methods are quite similar. Compositions  $A$ ,  $C$ , and  $G$  (Fig. 1) can be grown with ease. Growth of compositions such as  $XY_m$  have not been reported but are probably possible between points  $E$  and  $O$  (Fig. 1). Recent studies have been made of the growth of crystals from compositions such as  $D$  (Fig. 1).

A recent attempt by Pankove (6) to

grow germanium from an indium-germanium melt was also unsuccessful; it resulted in a type of epitaxial growth (myriads of commonly oriented dendrites of germanium on the germanium seed). Such dendritic growth could be explained on the basis of too-rapid growth and/or inadequate agitation (diffusion-controlled growth).

Carman *et al.* (7) grew a silicon crystal from a silicon-gold eutectic melt using a zone-melting technique. In a horizontal boat, they arranged in order a silicon crystal seed, the eutectic melt (6 percent Si at 370°C), and a quantity of silicon across the boat. A narrow zone of eutectic melt (achieved by using a single coil of an induction heater) joined the silicon seed and the source material. Within this zone, silicon was dissolved from the source material and deposited on the seed. By moving the zone at a rate of 0.001 inches per hour, they grew a crystal. In this experiment, apparently, conditions for good diffusion with the zone and on the growing face must have been present.

Crystal growth from water solution is accomplished from compositions identical with isopleth  $D$  (Fig. 1). Successful growth is obtained by providing proper control of agitation and supersaturation. It is evident that failure to obtain good growth from such compositions as  $D$  (Fig. 1) for higher temperature melts must be explained on the basis of inadequate controls.

Some water-soluble crystals are difficult to grow from water solution—for example, the alkali halides ( $\text{NaCl}$ ). Their solutions are characterized by poor supersaturation. Growth of the alkali halides can be catalyzed by the use of additives (8).

### Flux Melt Growth

Composition  $D$  (Fig. 1), although it is not ideally suited to growth by the crucible or withdrawal method, was used as early as 1823 by Berthier for growth of small crystals of the pyroxenes and olivines. If one can find a low-melting compound such as the alkali halides, borates, boron oxide ( $\text{B}_2\text{O}_3$ ), and so forth which form a eutectic with a refractory compound, then, by suitable choice of composition  $D$  (Fig. 1), it is possible to obtain recrystallization of the refractory compound.

In practice, one would pick a composition yielding the desired compound as the primary phase (in the field  $BCO$  of Fig. 1,  $XY_n$  is the primary phase for all compositions), which is allowed to nucleate  $XY_n$  and then is slowly cooled, allowing the nuclei of  $XY_n$  to grow to the solidus  $1BI$ , when all liquid would be solidified.

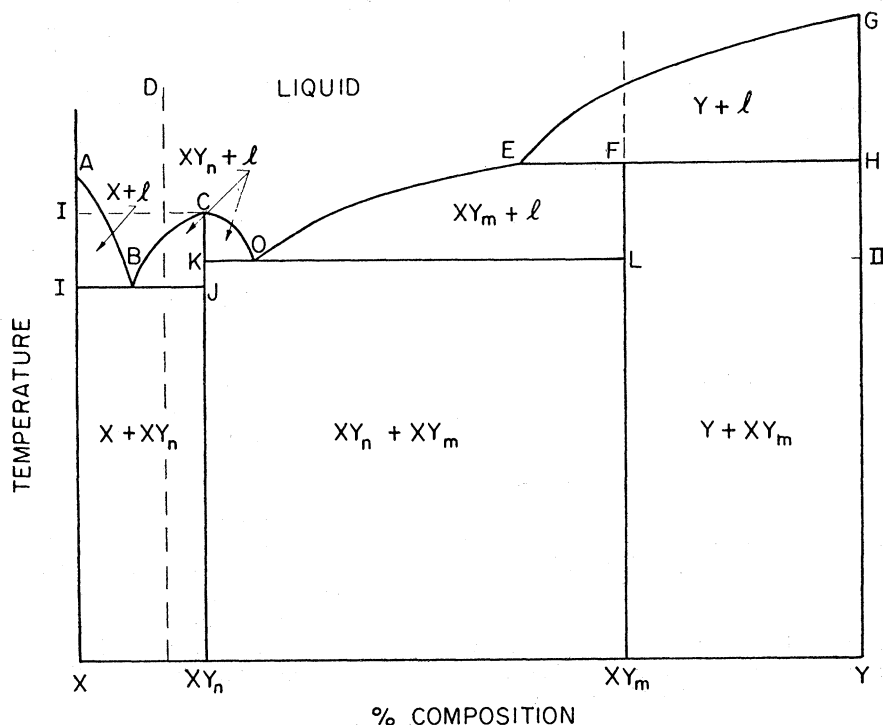


Fig. 1. Typical phase equilibrium diagram showing one congruent and one incongruent melting compound.

Weyl (9) used potassium chloride (KCl) to recrystallize magnesioferrite ( $\text{MgFe}_2\text{O}_4$ ). There are numerous other uses of fluxes in industry to recrystallize refractory compounds.

Nepheline ( $\text{NaAlSi}_3\text{O}_8$ ) is not in equilibrium with its own melt and hence cannot be grown directly from a dry melt. Winkler (10) has used lithium fluoride ( $\text{LiF}$ ) as a flux to produce single crystals of nepheline. The  $\text{LiF}$ -nepheline system is not a simple eutectic. However, a melt can be chosen which yields nepheline as a primary phase. The resulting crystals were imperfect and contained numerous inclusions.

Attempts to grow tetragonal barium titanate ( $\text{BaTiO}_3$ ) from its own melt have been unsuccessful, apparently because of the existence of higher polymorphic forms. Remeika (11) has succeeded in growing tetragonal  $\text{BaTiO}_3$  from a potassium fluoride (KF) melt. The  $\text{BaTiO}_3$ -KF system has been shown to be a simple eutectic system. In practice Remeika used a batch of 30-percent  $\text{BaTiO}_3$  and, after soaking the melt at 1150 to 1200°C for 8 hours to effect solution, he cooled the melt slowly to 850°C to effect crystallization. Separation of crystal and melt can be made by decantation of the supernatant melt or subsequent water extraction when cold. The yield consisted of crystal plates of  $\text{BaTiO}_3$  up to 1 square centimeter in area.

Three considerations enter into the choice of flux: (i) The necessary solubility (eutectic relation between compound and flux) between flux and refractory constituent at temperatures yielding the desired phase. Thus, in the case of  $\text{BaTiO}_3$  previously cited, the growth took place in the neighborhood of 1200°C within the field of stability of the tetragonal polymorph. Growth from its own melt yielded a higher temperature polymorph. (ii) Absence of reaction or solid solution between flux and compound. In the  $\text{LiF}$ -nepheline system a proper choice of composition must be made since the system contains another binary solid phase. Attempts at the Naval Research Laboratory to grow  $\text{MgFe}_2\text{O}_4$  with  $\text{B}_2\text{O}_3$  as the flux were unsuccessful. The attempt yielded a reaction product of a magnesium-iron borate not unlike natural ludwigite. Attempts at the Naval Research Laboratory to grow potassium bromide (KBr) crystals from a melt of potassium bromide and silver bromide ( $\text{AgBr}$ ) (simple eutectic) yielded only cloudy crystals. Although the  $\text{KBr}$ - $\text{AgBr}$  is reported as a simple eutectic system, there is a trace of solid solution at the liquidus; this solid solution unmixes on cooling to give a clouded crystal of KBr. (iii) It is desirable to be able to separate crystals from eutectics after growth; hence a water-soluble flux is ideal. These

considerations are another way of saying that a knowledge of the phase diagram is essential to complete success in flux melt growth.

In summary it must be repeated that growth by this method is largely diffusion-controlled since adequate stirring is rarely practical. Nucleation in this case is also quite a random process.

### Flame Fusion Method

The Verneuil Method (12) (flame fusion) has been used to grow refractory compounds such as corundum ( $\text{Al}_2\text{O}_3$ ), spinel ( $\text{MgAl}_2\text{O}_4$ ) and rutile ( $\text{TiO}_2$ ).

The source of heat is an oxyhydrogen torch. The method consists of passing the powder through the inner element of the torch. As the powder emerges into the flame, it is heated and collected on a refractory rod. By suitable manipulation, the mass of powder particles and liquid on the refractory rod are converted into a single crystal. A seed can also be used as the collecting rod.

As in the previously described crucible and withdrawal methods, the flame-fusion method requires that the crystal and melt be identical with respect to composition. With one exception, all crystals grown by this method have congruent melting points. The specification with respect to purity is extreme because the method does not lend itself to gross rejection of impurities during growth. Growth takes place on the thin skin of molten material atop the refractory support. If this liquid layer becomes clouded with foreign material rejected during crystallization, further addition of material is impeded and further good growth is halted. As the powders pass through the flame to their destination, they acquire heat but quite probably are not melted until contact with the growing surface is made. Then they melt and become part of the thin liquid layer on the growing crystal. This fusion and subsequent crystallization on the substrate takes place in an enormous thermal gradient. Only ideal chemical homogeneity permits single-crystal growth under these conditions.

Star sapphires have been produced by using a composition of  $\text{Al}_2\text{O}_3$  with a trace of  $\text{TiO}_2$  which is stable and homogeneous under the conditions of growth but which when annealed precipitates  $\text{TiO}_2$ . The precipitate, under controlled conditions, occurs on the principal crystallographic planes of the single sapphire crystal, thus yielding veils of  $\text{TiO}_2$  oriented to present the optical star effect (13).

The case of spinel growth is complicated by the experience that it is difficult to grow  $\text{MgAl}_2\text{O}_4$  on composition. This difficulty is reduced by growing the solid

solution of  $\text{MgAl}_2\text{O}_4$ - $\text{Al}_2\text{O}_3$  with compositions up to 80 mol percent  $\text{Al}_2\text{O}_3$ . The resultant crystal is not stable at room temperature since annealing at lower temperatures causes exsolution (precipitation) of  $\text{Al}_2\text{O}_3$  (14). In an attempt to remove the strain, these crystals were annealed just below the liquidus and then quenched. In this procedure, the strain developed during growth was relieved without inducing exsolution. Rutile ( $\text{TiO}_2$ ) has been grown by flame fusion. The resulting boule, although it is of rutile phase, is deficient in oxygen ( $\text{TiO}_{2-x}$ ). It is opaque and has a high dielectric constant (15). Subsequent heating of the boule in  $\text{O}_2$  at 1000°C will reduce the  $\text{O}_2$  deficiency and return the boule to the transparent  $\text{TiO}_2$ . The oxidation-reduction process is reversible.

Scheelite ( $\text{CaWO}_4$ ) and powellite ( $\text{CaMoO}_4$ ) can be grown by flame fusion. However, if the feed material is on composition, growth is difficult since tungsten trioxide ( $\text{WO}_3$ ) and molybdenum trioxide ( $\text{MoO}_3$ ) are volatilized preferentially (16). Compensation for this volatilization can be made by adding excess oxide to the feed. No solid-solution growth is involved in this case, and excess oxide over that required for stoichiometry is simply volatilized. Similar compensation must be made in the case of the growth of nickel and cobalt ferrites. In these cases ferric oxide ( $\text{Fe}_2\text{O}_3$ ) is volatilized preferentially. Single crystals of these compounds can be grown but not on 1 to 1 molar composition. These ferrites can dissolve excess  $\text{Fe}_2\text{O}_3$  in solid solution.

Bauer (17) has grown mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) by flame fusion. This is the only published example of an incongruent melting compound grown by flame fusion or other methods. The  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system has one compound mullite (72 percent  $\text{Al}_2\text{O}_3$ ) melting incongruently at 1810°C to yield a liquid of 55 percent aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and crystals of corundum ( $\text{Al}_2\text{O}_3$ ). The shape of the liquidus is like that of Fig 1 over  $XY_m$ .

Normally, when one cools a melt of mullite composition at a temperature of about 1950°C, crystallization occurs with corundum as the primary phase, as in the case of  $XY_m$  (Fig. 1). With further cooling, corundum continues to precipitate until the peritectic at 1810°C is reached, when, at constant temperature, resorption of corundum by the liquid takes place, yielding mullite. In the flame-fusion growth of mullite, this precipitation of the primary phase corundum is bypassed and mullite forms. This crystallization takes place in a thermal gradient of several hundred degrees per centimeter. Attempts at the Naval Research Laboratory to grow another in-

congruent melting compound,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  were unsuccessful. This compound differs from mullite in that the liquidus overhead rises very steeply so that the separation of liquidus and peritectic is about  $165^\circ\text{C}$ , whereas the separation in the case of mullite is  $130^\circ\text{C}$ . Perhaps a requirement for the mullite growth was the fairly flat liquidus curve and the smaller separation of liquidus and peritectic isotherms.

## Solid Solutions

In the previous cases, the liquidus for the various systems was discontinuous—that is, interrupted by eutectics, compounds, or peritectics; the discontinuity defined areas of discrete phase stability. Another type of single-crystal growth involves cases where the liquidus is continuous and one phase—a solid solution—is in equilibrium. A typical diagram is given in Fig. 2. The liquidus and solidus lines are the loci of all compositions of liquid and solid in equilibrium at any temperature. At  $T_1$ , a crystal of composition  $C_1$  is in equilibrium with liquid  $C_1'$ . On cooling, the crystal first separating is richest in the more refractory phase. As cooling proceeds under equilibrium conditions, this first crystal must be made over by the liquid—dissolved and recrystallized—to attain the equilibrium concentration demanded by the new temperature condition. Thus, through a theoretical equilibrium cooling, the following sequence of steps would occur on cooling a composition  $X$ : (i) ( $T_1$ ) first crystal of composition  $C_1$  in equilibrium with liquid  $X$ ; (ii) on cooling to  $T_2$ , crystal  $C_1$  has dissolved and recrystallized to a crystal of composition  $C_2$  (containing less  $A$  than  $C_1$ ) while liquid  $X$  has lost  $A$  to become composition  $C_3'$ ; (iii) ( $T_4$ ) by this process, the last bit of liquid of composition  $C_4'$  is crystallized to yield a homogeneous solid-solution phase  $C_4$ .

Thus, under equilibrium conditions, the liquid of composition  $X$  is crystallized to a homogeneous solid of composition  $X$ . Failure of equilibrium crystallization will result in fractionation—the initial crystals will be richer in  $A$ ; the final crystals richer in  $B$ . In terms of single-crystal growth, this will yield a chemically zoned crystal (cored) so commonly found among the natural feldspars, pyroxenes, and other minerals. From the standpoint of material for solid-state physical investigation, such a badly cored or zoned crystal is extremely undesirable. For example, if by the crucible method we start with a charge of 5 mol percent of  $\text{AgCl}$  in  $\text{NaCl}$ , the system  $\text{AgCl-NaCl}$  shows continuous solid-solution relation of the liquidus. If we grow such a charge, the resultant

boule may be single but will have a composition at the tip of roughly 98 percent  $\text{NaCl}$  and, for example, along a 3-inch length will vary in composition continuously to 90 mol percent  $\text{NaCl}$ . Using the crucible or withdrawal technique as usually practiced, it is virtually impossible to obtain a chemically homogeneous, solid-solution single crystal. One unique exception to this statement is the case of KRS-5. The system thallium triiodide ( $\text{TlI}_3$ )-thallium tribromide ( $\text{TlBr}$ ) forms a continuous series of solid solutions, but the liquidus shows a low melting minimum at 42 mol percent  $\text{TlBr}$ . Single crystals of this composition have been grown and shown to be homogeneous.

The solubility of a foreign ion or solute in a melt and in the solid phase in equilibrium with that melt on crystallization is usually not identical. Forces acting within the growing solid tend to deny access to all of the ingredients of the mother liquor. This phenomenon has been used for years in the purification or separation of closely allied materials. As in the previously mentioned case of  $\text{NaCl-AgCl}$  melts, the operation of crystal growth results in a disproportioning of the original homogeneous solution into a continuously chemically graded solid solution. By repeated growth of the extreme portions of such a chemically graded system, one could slowly purify a mixed melt of the solute just as one extracts soluble salts in an analytic filtration by washing with distilled water. Although the method of purification by crystal growth has been known for a long time, the refinement of the process has taken place with the advent of the growth of single-crystal germanium and the purification of germanium or silicon by zone refinement. Zone refining is a process involving the localized melting of a thin zone of an ingot and the movement of this melted zone slowly along the

length of the ingot. In practice, one would melt the end of the ingot and then slowly move the zonal heat source (or the ingot) along the length, allowing the passed material to freeze. In this operation, if the impurity distribution is in the direction of the liquid (if the crystallized material rejects the impurity), then the liquid zone will accumulate the impurity naturally, and the impurity is segregated in the final zone. In a solid solution system, there is a distribution solid-liquid and complete sanitation is never achieved. This distribution is defined as the ratio of the concentration in the initial melt to the concentration in the first crystal, but it varies in an as-yet-unexplained fashion from ion to ion and host to host (18).

The result of the crystallization of a melt in a solid-solution system is a solid whose composition varies continuously from the initial crystal deposited to final exterior of the crystal. One can obtain a single crystal of widely varying composition interior to exterior (the initial freezing is richest in the more refractory constituent). If during the freezing there are times when near equilibrium is obtained, the resultant crystal will be made up of zones corresponding to these terms. These zones may in themselves be chemically homogeneous—for example, plagioclase, feldspars in granites, and so forth.

It is difficult to explain the large chemically homogeneous single crystals of solid solutions that one finds in nature, such as tourmaline, topaz, olivine, and others. Perhaps time alone is the explanation for such chemical perfection.

In the laboratory, it is extremely difficult to obtain an unzoned or chemically homogeneous solid-solution ingot or crystal. Recently, as a result of the work on germanium and silicon, a new concept of zone-leveling has been introduced. In the course of zone melting of a solid-solution ingot, the initial solid crystallizing out will differ markedly from the liquid. As the zone melting progresses, a point will be reached where liquid and solid have the same composition. This portion of the solidified ingot will be chemically homogeneous since the composition of solids entering and leaving the zone is the same. Final portions of liquid, however, will have an enriched composition. Thus it is possible to obtain an ingot and, under certain conditions, a single crystal, a portion of which will be chemically homogeneous (19).

This discussion has been limited to binary systems. The more complicated ternary systems have not been discussed. However, the same general observations still apply. Congruent-melting ternary compounds can be grown as single crystal material from the melt—for example, synthetic phlogopite. The same limitations apply, however. For example, one

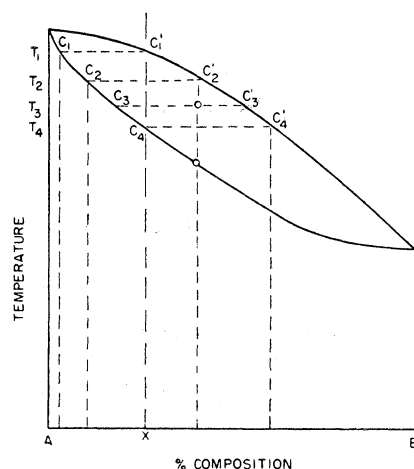


Fig. 2. Phase equilibrium diagram showing complete solid solution between the two components.

can synthesize chalcopyrite by sintering or solid-phase reaction, but quite probably it cannot be grown from the melt since it melts incongruently.

#### References and Notes

1. A single crystal is one that satisfies the external morphological, optical, and x-ray criteria for singularity. The criterion of singularity with respect to domain structure is not a mandatory specification.
2. I have drawn freely for my data on the experience of the staff of the Crystal Branch of the U.S. Naval Research Laboratory, includ-

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## Oceanography, Fisheries, and Atomic Radiation

In writing this report we have had four groups in mind—research administrators, statesmen, scientists, and the public. For those who have responsibility for the support of research, we have attempted to outline the scientific questions that need to be answered as a basis for intelligent policy, the means by which they can be attacked by classical research methods at the outset, and the broader problems of the oceans that can be hopefully attacked by the use of radioactive tracers. For the statesmen who have responsibility for national and international policy, we have attempted to formulate recommendations, based on our present small body of knowledge and our awareness of our larger area of ignorance, concerning the national and international actions and agreements that are necessary for the happy exploitation of the oceans in the new atomic age. For the scientists, we have attempted to summarize what is known about the actual and potential effects of radioactive materials in the oceanic realm and the interest of marine scientists in these substances. For the public, to which we all belong when we are outside our own specialties, we have summarized the levels of calculated risk that must be balanced against the wonderful promise of atomic energy for the welfare of mankind.

### How Does the Atomic Energy Program Affect the Oceans?

We have considered three aspects of the atomic energy program that directly

involve the oceans and, therefore, the marine sciences: weapons tests over or in the sea, disposal of radioactive wastes from nuclear power plants, and the use of radioactive substances in increasing our understanding of the oceans and of the creatures that live in the sea. These different aspects cannot easily be separated. Weapons tests and the disposal of radioactive wastes present great opportunities for studying the oceans. On the other hand, increased knowledge of the oceans is essential to avoid or minimize the destruction of marine resources in the development of atomic energy.

The continuing development of atomic energy will produce progressively greater amounts of radioisotopes, and with them greater amounts of radioactive waste material. Since the oceans cover 71 percent of the earth, and ultimately receive the drainage from the land, they are the principal reservoir where radioisotopes will finally accumulate. Relatively small quantities are now being added to the surface waters of the ocean as fallout from weapons-testing programs, and in a few places as waste materials.

When nuclear reactors for the production of power are put into large-scale operation, as they certainly will be in the foreseeable future, the oceans will be seriously considered for the disposal of large quantities of wastes. Even if direct and intentional disposal at sea is not practiced, reactors may be built along sea coasts or on rivers near large population centers, and accidental pollution may occur.

The problem of disposal of radioac-

tive wastes is similar in character to, though potentially far greater in scope than, other problems of pollution. An object lesson can be drawn from our experience with the disposal of human and industrial wastes in inland water bodies and coastal waters and with the smog problem that afflicts many of our large cities. During the early stages of the growth of industries and populations in cities, wastes were added to nearby lakes or bays, and to the air, in what seemed at the time to be innocuous quantities. As a matter of fact, the quantities were small enough to be purified by natural processes. In the course of time, however, the quantities increased insidiously so that today many natural waters cannot purify themselves and without expensive treatment are dangerous to human beings.

In almost every case the problem was ignored until it had become formidable in magnitude. Short-range solutions were employed, based on inadequate knowledge, special interest, and what we now know was an unfounded confidence in the capacity of the atmosphere and the waters to absorb noxious substances. As a result, unnecessary damage was done to human beings and their environment. Much of this could have been avoided if an adequate program of scientific investigation had been started sufficiently far

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This article is the text of the summary report of the Committee on the Effects of Atomic Radiation on Oceanography and Fisheries. The report is part of a continuing study on the Biological Effects of Atomic Radiation conducted by the National Academy of Sciences with the support of the Rockefeller Foundation. The members of the committee are Roger Revelle, Scripps Institution of Oceanography, chairman, Howard Boroughs, University of Hawaii; Dayton E. Carritt, Johns Hopkins University; Walter A. Chipman, U.S. Fish and Wildlife Service; Harmond Craig, Scripps Institution of Oceanography; Lauren R. Donaldson and Richard H. Fleming, University of Washington; Richard F. Foster, General Electric Company; Edward D. Goldberg, Scripps Institution of Oceanography; John H. Harley, U.S. Atomic Energy Commission; Bostwick Ketchum, Woods Hole Oceanographic Institution; Louis A. Krumholz, American Museum of Natural History; Charles R. Renn, Johns Hopkins University; M. B. Schaeffer, Scripps Institution of Oceanography; Allyn C. Vine, Woods Hole Oceanographic Institution; Lionel A. Walford, U.S. Fish and Wildlife Service; and Warren S. Wooster, Scripps Institution of Oceanography. Subheads have been inserted in the text. The full report will be published in monograph form by the NAS.