

# The Phenomena of Crystallization and Melting, and the Internal Structure of Liquid of a Simple Substance

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## Abstract

The cybotactic group or the cybotactic crystal in a liquid is thought to be formed by chance in a liquid by sudden grouping of some number of free liquid molecules. Thus the equilibrium between the cybotactic groups and the free liquid molecules can be maintained at any temperature, by changing their relative amounts. This is entirely different from the equilibrium between the adult crystals and their melt, and a simple explanation was looked for. Latent heat of fusion per one constituent molecule is supposed to be much smaller with cybotactic crystals than that of the ordinary adult crystals, and consequently the melting point in the former case is much lower. By considering that the size of a cybotactic crystal is of the order of the unit cell of the crystal, the mechanism of the formation of the crystal nuclei and their growth in a super-cooled liquid is discussed. Anomalous behaviour of liquid water in its specific volume and its viscosity was ascribed to the presence of the cybotactic ice-crystals in liquid water, and a rough amount of the cybotactic ice-crystals was estimated by making use of the temperature dependence of its specific heat and specific volume. To explain the results of the X-ray diffraction with liquid the presence of various kinds of cybotactic groups consisting of different number of constituent molecules was considered. An amorphous solid or the glassy state of a substance was supposed to consist mainly of cybotactic groups, containing some free molecules distributed at random. Beilby layer on polished metal surface was considered to consist of the amorphous solid in the cybotactic sense. Some modification of the theory of recrystallization of metal, proposed previously by the writer and Koyanagi, was made by introducing the idea that the melting point of very fine crystals is much lower, and that at numerous localities in the metal it is transformed to the state of amorphous solid by cold working or by annealing.

## Introduction

When a crystal is heated it melts abruptly and completely at its melting point, and we can not heat it above this temperature while keeping it unaltered in the crystallized state. Reversely, when the liquid of the same substance is cooled the circumstances are somewhat different. Usually it crystallizes abruptly and completely at its freezing point which is the same as the melting point of the substance, but in the case of many substances we can, with some care, cool it to a

temperature below its freezing point, producing a super-cooled liquid. The crystallization of the melt without seed crystals takes place only by the growth of the crystal nuclei, which are formed spontaneously here and there in the melt in the super-cooled state. Thus when the nuclei are too scant in number or when their growth is much retarded by some conditions, as when they are too much cooled, the crystallization does not occur; and the melt remains super-cooled for a long time. When we speak of the fusion of crystals, we refer usually to adult crystals which are enormously larger than their nuclei; and the fusion of such crystals takes place on all parts of their boundary surfaces simultaneously, and never at the interior of the crystal.

### Cybotactic Group and the Adult Crystal

Some years ago the writer<sup>1)</sup> proposed a theory that a great number of tiny ice-crystals having the size of the order of the unit cell of the ice-crystal are present in liquid water. These tiny ice-crystals are supposed to be unstable and of only temporary existence: a few number of molecules of water unite together to form the crystal lattice only over very short elements of space and time. However the total quantity of such tiny ice-crystals will be determined by the temperature, and it will decrease with rise of the temperature. By taking this fact into consideration, anomalous behaviour of liquid water in its specific volume and viscosity was explained. To clarify the manner of molecular aggregation in liquids the method of X-ray diffraction has been adopted by many workers; and many of them inclined to assume the presence of some kind of pseudo-crystallinity in liquids, a state of temporary arrangement of molecules, very probably similar to that which exists in the solid state. Stewart<sup>2)</sup> called such temporary pseudo-crystalline arrangement of molecules in liquid "Cybotaxis". This conception of cybotaxis is similar in general to the writer's idea mentioned above. Though strictly, a distinction must be made between them as will be shown later; but for the present, we regard them as the same in the sense that a spontaneous and unstable aggregation of a certain small number of molecules in a certain manner of configuration occurs momentarily here and there in the liquid in statistical way, and we consider about the equilibrium between the number

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1. U. Yoshida: *These Memoirs*, A, **19**, 271 (1936).

2. Stewart: *Rev. Modern Physics*, **2**, 116 (1930).

of cybotactic groups and the remaining part of the liquid whose molecules are supposed to be free and not aggregated.

Let the total number of liquid molecules in unit volume be  $N$  including both free and aggregated ones, and the number at a certain temperature of the cybotactic groups in unit volume each consisting of  $x$  molecules by  $n$ ; then the total number of free molecules in unit volume will be  $N-xn$ . Among these a certain fraction  $\alpha$  per unit time will aggregate to form the cybotactic groups, and at the same time a certain fraction  $\beta$  of the cybotactic groups per unit time will decompose into free molecules. Thus, in equilibrium, we have

$$\alpha(N-xn) = \beta xn, \dots \dots \dots (1)$$

$$\therefore n = \frac{1}{1 + \frac{\beta}{\alpha}} \frac{N}{x} \dots \dots \dots (2)$$

In this equation both  $\alpha$  and  $\beta$  depend upon the temperature, the number of the constituent molecules  $x$  in one cybotactic group and the difference of the potential energy  $\phi$  per one molecule in arranging in the cybotactic group which may depend indirectly upon the number of constituent molecules. However, for a given kind of cybotactic group in a given liquid, the last two factors are constant, and both  $\alpha$  and  $\beta$  depend only upon the temperature. With increase of temperature  $\alpha$  will decrease and  $\beta$  will increase continuously in consequence of the increase of the kinetic energy of molecules; and thus  $n$  will decrease continuously with increasing temperature. This is entirely different from the melting of an adult crystal of a substance into its liquid and the freezing of the liquid on the surface of the adult crystal at its melting point, which take place only at that temperature: i. e. the adult crystal and the liquid of a substance can co-exist only at its melting point, and not at any other temperature. The melting and the freezing in this case take place as has been stated before only at the surface of the adult crystal having a considerable thickness; and thus both the surface density of the molecules constituting the crystal lattice at the boundary surface which are to be dissolved into liquid and that of the liquid molecules which are to be frozen on the surface of the crystal are respectively constant regardless of time and the quantities of the crystal and the liquid. Let  $N_c$  be the surface density of the liquid molecules at the surface of the crystal and  $N_c'$  be that of the molecules of the crystal at its boundary surface,

which correspond to  $n\alpha$  in equation (1). Then in equilibrium we obtain, instead of the equation (1),

$$\alpha N_i = \beta N_e, \dots\dots\dots(3)$$

which means that the number of molecules which freeze from the liquid to the crystal is the same as that of the molecules which dissolve from the crystal to the liquid, and represents the condition of equilibrium between the crystal and the liquid at the melting point. When temperature is raised even slightly the mean kinetic energy of the constituent molecules in the crystal increases, and the number of the constituent molecules at the crystal boundary whose kinetic energy is greater than is necessary to separate a molecule from the crystal lattice, will become greater. Consequently the value of  $\beta$  increases with temperature. On the other hand, the difficulty of entrapping into the crystal lattice the liquid molecules will become greater with rise of the temperature, due to the increase in their kinetic energy; and consequently the value of  $\alpha$  will become smaller with increasing temperature. Thus when the temperature is raised even slightly above the melting point, the right hand side of the equation (3) will become greater than the left, showing that the melting of the crystal proceeds continuously until the entire dissolution of the crystals is reached so long as the temperature is kept higher than the melting point. On the contrary when the temperature is kept even a little below the melting point, the freezing of the liquid goes on until the whole liquid is frozen.

In the case of the cybotaxis the number  $n$  of the cybotactic groups per unit volume of the liquid changes continuously with the temperature, and the equilibrium at various temperatures between the cybotactic groups and the free molecules of the liquid is maintained by changing the number of groups as is shown by the equation (2). On the contrary, the surface density of the molecules of the adult crystal and of the liquid at their contact surface, which take part in fusion and freezing, are constant irrespective of the temperature, and the transformation from solid to liquid or vice versa at a temperature other than the melting point can not be balanced to attain an equilibrium as in the case of the cybotaxis. After all, the discontinuous transformation of an adult crystal of a substance to its melt or vice versa at its melting point owes its origin to the fact that it is a surface phenomenon at the crystal boundary, and not at the interior of the crystal,

just as is the case in vaporization and sublimation. The freezing of the liquid of a substance to its crystal, starting from the crystal nuclei, takes place at the very commencement of freezing and sometimes also at a state when the growth of the adult crystals is going on. According to the writer's view the crystal nuclei are nothing but the crystals themselves grown already to a tolerable size as compared to the cybotactic unit cell, though they are still small when considered macroscopically. Thus they are not of spontaneous and unstable existence, and can maintain their crystalline state even at a temperature just below the melting point of the substance. As we may consider their outer surface too in this case, the circumstances are entirely the same as in the case of adult crystals. They have the same power of growth and dissolution respectively at the temperature below and above the melting point as the adult crystals, though the velocity of their growth and dissolution are very much less than those of the adult ones, due to the smallness of their outer surface.

### Latent Heat of Fusion and the Melting Point

The latent heat of fusion of the crystal of a substance relates mainly to the work necessary to transfer a constituent molecule of the crystal, which is situated at the crystal lattice on its outer surface, into its melt at its melting point. This work is the same as the difference between the potential energies of the molecule situated in the two different positions. In order to overcome this potential drop, kinetic energy of the constituent molecule due to thermal agitation must exceed it. Thus when this potential drop is great, the melting of the crystal requires a high temperature. This means that the greater the molecular latent heat of fusion of a substance the higher is its melting point. The law that the atomic latent heat of fusion of a substance is proportional to its melting point expressed in absolute temperature is already known to be obeyed roughly by many substances, and is treated theoretically by many authors.<sup>1)</sup> This law is obeyed better by the metals,<sup>2)</sup> and rather satisfactorily by the metals having the crystal lattices of the face-centered cubic and of the hexagonal closed packed, in which the metals are known to have almost the same relative inter-

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1. F. A. Lindemann: *phys. ZS.*, **11**, 609, (1910); E. Grüneisen, *Verh. d. D. phys. Ges.*, **14**, 330, (1912); W. Braunbeck, *Z. S. f. Phys.* **38**, 549, (1926), etc.
  2. I. H. Richards, *Chem. News*, **75**, 278, (1897).

atomic arrangement. The same law for the boiling point is also valid for many substances and is known by the name of Trouton.

The attractive force of a crystal for an atom or a molecule at its surface to fix the latter into its lattice point will be very much weakened when the size of the crystal is so reduced that it can only exist in the cybotactic state, by reason of the small number of the attracting atoms in the crystal; and the potential drop, against which some

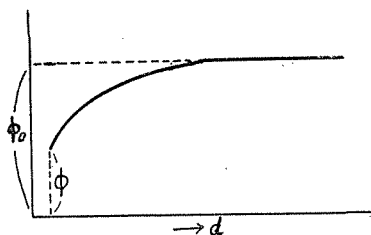


Fig. 1

amount of work is needed to transfer the atom or the molecule from the crystal lattice into the liquid, becomes smaller. This relation between the potential drop  $\phi$  and the linear size  $d$  of the crystal is shown schematically in Fig. 1. The value of  $\phi$  will increase at first with the linear size of the crystal, and will attain a maximum which

is the same as that of the adult crystal. If this consideration is correct, the latent heat of fusion of the crystal will be much smaller with very tiny crystals such as cybotactic ones, as compared with that of the adult crystal. According to the law stated above, showing the relation between the latent heat of fusion and the melting point, which must be considered to be strictly valid for the same substance in this case, the decrease of the latent heat of fusion with cybotactic crystals means that their melting point becomes much lower than the ordinary value as was pointed out by Meissner<sup>1)</sup> for microscopic crystals. The cybotactic groups are of only spontaneous and statistical existence, and the meaning of their melting point is somewhat different from the ordinary: At the melting point the mean kinetic energy of the molecules due to thermal agitation is the same as the value of  $\phi$ ; at a higher temperature the probability or chance for the formation, existence and growth of the cybotactic groups lessens and at a temperature lower than their melting point this probability or chance increases. When a cybotactic crystal in a super-cooled liquid has grown somewhat by chance even at a temperature higher than its original melting point, its melting point rises correspondently, and the chance for its further growth is increased more than before. If this happens actually, then its melting point rises again and causes a still further

1. Meissner: *Z. S. f. anorg. Chem.*, **110**, 169, (1920).

increase in chance for further growth. This tendency to the formation and growth of the cybotactic crystals will be greater, of course, than that of becoming thinner or of dissolution into free liquid molecules, at a temperature lower than their melting point, and a rapid crystallization of the whole liquid will occur in this case.

### Formation of the Crystal Nuclei and their Growth in a Super-cooled Liquid

If some of the cybotactic crystals in a super-cooled liquid have grown, by chance in the way stated above, to such a size that their melting point is higher than the temperature of the liquid, their stability and the tendency to grow increase more and more one-sidedly, until adult crystals of sufficiently large size are formed in the liquid. Thus the crystal nucleus in a super-cooled liquid is nothing but a submicroscopic crystal which has grown from a cybotactic crystal to such a size that it is already permanently stable and is not in danger at that temperature of being decomposed abruptly by thermal agitation. According to Tammann<sup>1)</sup> and others, the number of the crystal nuclei formed spontaneously in a super-cooled liquid attains a maximum at a temperature far below the melting point of the substance, and decreases again with further decrease of the temperature. As this decrease beyond the maximum is ascribed to the enormous increase of viscosity of the liquid at such low temperature, we may consider generally that the chance of the spontaneous formation of the crystal nuclei is more and more favoured with decrease of the temperature, if the effect of increasing viscosity is disregarded. This temperature dependence of the formation of the crystal nuclei is well explained by the idea above stated on the growth of the cybotactic crystals in the super-cooled state. The chance of formation of the cybotactic unit crystals increases with decreasing temperature, i. e. with decreasing kinetic energy of the liquid molecules. An enormous increase of viscosity with decreasing temperature in the super-cooled state thus seems to be due to the increase in number of the cybotactic crystals. If we assume that the growth of the cybotactic crystal is mainly caused by the unification of free molecules of the liquid to the cybotactic crystals existing at that moment, the growth will be retarded at very low temperature by the want of uniting free molecules. This way

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1. Tammann: *Kristallisieren u. Schmelzen*, p. 151, (1903).

of explaining the decrease of the number of the crystal nuclei at very low temperature is likely to be more reasonable than to ascribe it merely to the increased viscosity.

When crystal nuclei have been formed in a super-cooled liquid, they have already acquired a permanent stability in all temperatures below the melting point of the substance, and the change for them is now only toward their growth even up to adult crystals, so long as the temperature is maintained below the melting point. The rapidity of the crystal growth in this state will of course be retarded by the increase of the temperature due the increase of the kinetic energy of the molecules, but at the same time it will be accelerated by the increase of the free molecules colliding on the surface of the crystal with increasing temperature. The fact that the temperature of the maximum rapidity of the crystal growth in the super-cooled liquid is rather shifted toward a temperature higher than that corresponding to the formation of the maximum number of crystal nuclei suggests that the presence of the latter factor influences the crystal growth. If this reasoning be correct, a cybotactic group which is to be developed to a crystal nucleus and even to an adult crystal must have at its birth the same crystal lattice as the adult one. This is somewhat different from the idea of the "pseudo-crystalline" arrangement of the molecules which has been adopted by other authors, and is distinguished by the writer by calling it "cybotactic crystal". According to the writer's view there are many kinds of cybotactic groups, consisting of various numbers of constituent molecules. When the number of constituent molecules is too few, for example two or three, it is insufficient to form a unit cell of the crystal. To form a unit cell of the body-centered cubic, 9 atoms are necessary, and for that of the face-centered cubic 14 atoms are needed. Thus the cybotactic crystal which has the ability to grow to the crystal nucleus must contain at least the number of constituent molecules or atoms of this order.

### Cybotactic Crystals in Liquid Water

In the former report<sup>1)</sup> the writer has assumed that the cybotactic ice-crystals have the same latent heat of fusion and the same specific volume as those of the adult crystal respectively. But in the present case, the writer has assigned a much smaller value of the latent heat

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1. loc. cit.



of fusion to the cybotactic crystals. Water has a peculiar property of expanding by freezing, and consequently that its melting point decreases with increasing pressure. Parallel with these, the specific volume of liquid water has a minimum at  $4^{\circ}\text{C}$ , and increases with decreasing temperature below this point. This temperature of minimum specific volume becomes lower with increasing pressure<sup>1)</sup>, and the presence of the minimum becomes almost insensible at the pressure of about  $2000 \text{ Kg/cm}^2$ . The change of viscosity of liquid water with pressure<sup>2)</sup> behaves anomalously also at temperatures below about  $30^{\circ}\text{C}$ . Below about  $30^{\circ}\text{C}$ , the viscosity decreases at first with increasing pressure, attains a minimum, and then increases again with the increase of pressure. If we assume the presence in liquid water, of cybotactic ice-crystals whose specific volume is the same as that of ordinary ice, the specific volume of liquid water will become smaller with increasing temperature, by the diminution of the total number of the cybotactic crystals, and at the same time it will become greater by the thermal expansion with increase of the kinetic energy of the molecules. The predominance of the former effect at low temperature gives rise to the appearance of the minimum in the specific volume at  $4^{\circ}\text{C}$ ; and the diminution of number of the cybotactic ice-crystals with increasing pressure shifts the point of minimum specific volume toward the lower temperature. The presence of the cybotactic crystals, which are of course much larger than the free liquid molecules, will increase the viscosity, which will also increase with increasing pressure even when the internal structure of the liquid remains unchanged. Thus the presence of minimum in the viscosity of water at a certain pressure seems to be due also to the diminution of the number of the cybotactic crystals with the increase of pressure. The rate per one degree of temperature change of the diminution in number of the cybotactic crystals with increasing temperature, is considered to be greater at lower temperature, and this will have the effect of making the specific heat of the liquid especially higher at lower temperature than would be expected when no change in the internal structure of liquid occurs with change of the temperature. This is actually observed in the case of liquid water, where the specific heat is minimum at about  $35^{\circ}\text{C}$ . Thus, if we accept the presence of cybotactic ice crys-

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1. Bridgeman: *The Physics of High Pressure*, p. 143, (1931).

2. Hauser: *Ann. d. Phys.*, 5, 597, (1901); Bridgeman: *The Physics of High Pressure*, p. 347, (1931).

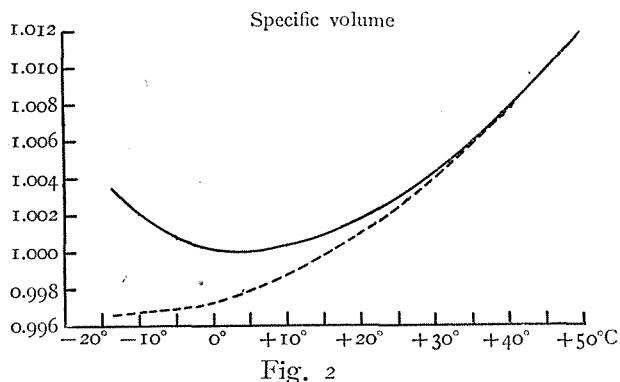
tals in liquid water, its anomalous behaviour is understood qualitatively.

The next problem is to estimate the quantity of the cybotactic ice-crystals. This is already investigated by the writer<sup>1)</sup>, and the value of 0.6 % at 0°C was obtained. The general principle in doing this is as follows: The specific volume and the specific heat of liquid water must increase gradually without any abnormality always with increasing temperature, if the effect caused by the presence of the cybotactic ice-crystals in liquid water is eliminated. In regard to the temperature dependence of the quantity of the cybotactic crystals the writer has assumed as before, that the quantity of cybotactic crystals can be represented by an exponential function of the temperature expressed in Centigrade. This is in conformity with Boltzmann's expression for the molecular aggregation, at least for a temperature range not very wide. Thus, for the quantity of the cybotactic crystals  $x$  at the temperature  $t$ , we have

$$x = x_0 e^{-at},$$

where  $x_0$  is the quantity of cybotactic crystals at 0°C, and  $a$  is a certain constant. The above formula will not be strictly correct for a very wide range of temperature, but it seems reasonable to consider it valid in showing the general tendency of the temperature dependence of the quantity of cybotactic crystals, because the formation and the decomposition of the cybotactic crystals are statistical phenomena.

In the previous report the writer assumed that the latent heat of fusion of the cybotactic ice-crystals is the same as that of the adult ice-crystals and adopted the value of 80 cal. per 1 gr. But this means



that the melting point of both the cybotactic and adult crystals is the same, and is 0°C; and this is inconsistent with the presence of the super-cooled state of liquid water. The logical con-

1. loc. cit.

sequence of the writer's consideration requires that in order for the super-cooled state of a liquid to be possible at a temperature below its freezing point, this temperature must be above the melting point of the cybotactic crystals, and this in turn requires that the latent heat of fusion of the cybotactic crystals is much less than that of the adult crystals. For the latent heat of fusion of the former the value of 16.3 cal. per 1 gr. was adopted in the present case, which corresponds to the melting point of  $-217.4^{\circ}\text{C}$ . Corresponding to this value of the latent heat of fusion of the cybotactic ice-crystals, the value of 3 % is taken as the quantity of the cybotactic crystals  $x_0$  at  $0^{\circ}\text{C}$ , which is about 5 times the value assumed in the former report; and the value of 0.063 is taken for  $\alpha$ . With these values those of  $x$  and  $\frac{dx}{dt}$

at any temperature are obtained by the exponential function before stated. The contribution of the cybotactic crystals to the specific volume and the specific heat of liquid water is respectively calculated in the same manner as before by considering the specific volume of the cybotactic and the adult ice-crystals the same; and the results

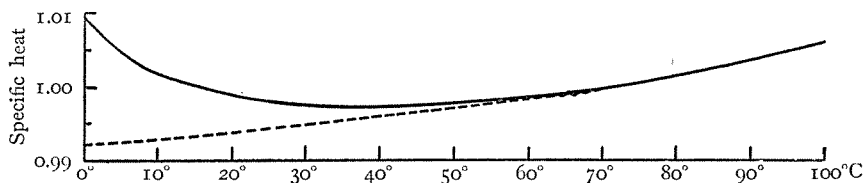


Fig. 3

are shown in Figs. 2 and 3, where the curves drawn in full lines represent the observation and those drawn in broken lines represent the specific volume and the specific heat of idealized liquid water obtained by eliminating the effect of the cybotactic crystals. These curves drawn in broken lines contain no minima, they run gradually without any abnormality always increasing with temperature even in the super-cooled state for the specific volume. This satisfies the conditions required by the idealized liquid water consisting of their free molecules only. At first sight, the above way of estimating the specific heat and the quantity of the cybotactic ice-crystals is entirely arbitrary. But actually this is not so. The writer carried out the same calculation with various values of  $x_0$ ,  $\alpha$  and the latent heat of fusion of the cybotactic crystals taken in a systematic manner, and found that with values other than those given above the conditions required by the idealized liquid water were not fulfilled so satisfactorily. Thus,

though the above estimation of the values of  $x_0$ ,  $\alpha$  and the latent heat of fusion of the cybotactic crystals may not be precise, it may be said to be of a proper order if the writer's view is reasonable.

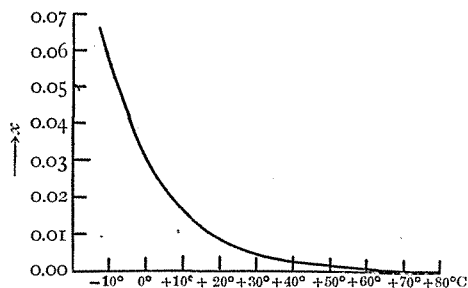


Fig. 4

The temperature dependence of the quantity of the cybotactic crystals in liquid water, which was calculated with the data estimated above, is shown by the curve in Fig. 4. The quantity increases from 0.5% at about 30°C to 6% at about -10°C when the temperature is lowered. The viscosity of the liquid water, as is shown by Fig. 5, increases roughly in the same proportion from the value of 0.008 at 30°C to 0.025 at about -10°C. Thus an enormous increase of viscosity with decrease of the temperature, at least in the above temperature range, seems mainly to be due to the increase of the cybotactic ice-crystals.

In the above discussion the writer assumed the presence of only one kind of cybotactic groups, i. e. the cybotactic ice-crystals having the same crystal lattice as the ordinary adult crystal. But it seems more probable that there are several kinds of cybotactic groups consisting of different numbers of molecules. According to Stewart<sup>1)</sup> the intensity maxima of the diffraction halo of the monochromatic X-rays due to liquid water can be traced from 2°C to 98°C. He found that the most prominent peak occurs at a gradually increasing angle as the temperature is raised, and that

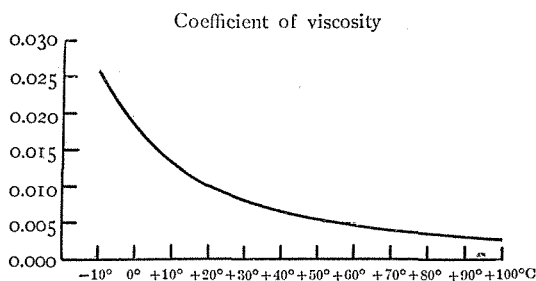


Fig. 5

the second peak occurs at smaller angles and finally disappears as the temperature is raised. Bernal and Fowler<sup>2)</sup> proposed the theory that there is a tendency for the molecular arrangement at low temperature below 4°C, to be tridimite-ice-like; at ordinary temperatures to be

1. Stewart: *Phys. R.* **37**, 9 (1931).

2. Bernal and Fowler: *J. Chem. Phys.*, **1**, 515 (1933).

quartz-like; and at high temperature, extending well below the critical temperature of  $374^{\circ}\text{C}$ , there is a tendency to be closed packed, the ideal type of liquid. This idea is the same in its main feature as the writer's. Relative amounts of different kinds of cybotactic groups will change continuously with temperature; and as the diffraction halo is the resultant caused by the mixture of these different kinds of cybotactic groups, the position of its peak will change continuously with temperature, due mostly to the change in their relative proportion. Now let us assume that the work per one constituent molecule which is necessary to decompose a group becomes greater with increasing number of constituent molecules in the group. Then the melting point of a given kind of cybotactic group will be higher with increasing number of constituent molecules in one group; i. e. the stability of the group will increase with increasing number of constituent molecules. On the other hand, the chance of formation of a cybotactic group will increase with decreasing number of constituent molecules. Consequently these circumstances will make the temperature variation of a cybotactic group consisting of a smaller number of constituent molecules much less than that of a cybotactic group consisting of a greater number of constituent molecules. Accordingly the cybotactic groups composed of larger numbers of constituent molecules will more and more prevail in quantity as the temperature is lowered; and on the contrary, those composed of smaller numbers of constituent molecules will become more and more predominant as the temperature is raised. This idea is in accord in general aspect with that proposed by Bernal and Fowler, who have assumed the presence, in liquid water, of three different kinds of cybotactic groups, differing in their relative amounts with different temperatures; and the cybotactic ice-crystals as was assumed by the writer correspond to the tridimite-ice-like groups considered by Bernal and Fowler. According to the writer's estimate, as is stated before, the amount of the cybotactic ice-crystals is small above  $0^{\circ}\text{C}$ , and has already fallen to 1 or 2 % at  $10^{\circ}\text{C}$ . Thus the diffraction halo which was observed by Stewart at temperatures as high as  $98^{\circ}\text{C}$  must be ascribed to the other cybotactic groups containing a smaller number of constituent molecules or to free water molecules distributed at random.

In calculating the specific volume and the specific heat of the idealized liquid water, the writer has paid attention only to the free molecules of water and the cybotactic ice-crystals having a size larger

than the unit cell of the ice-crystals, disregarding the presence of the other cybotactic groups composed of a smaller number of molecules. In these cybotactic groups composed of fewer molecules, the constituent molecules are thought to be united much more loosely than in the cybotactic ice-crystals; which is equivalent to saying that the latent heat of fusion per one molecule is much less in the former than in the latter. Moreover, it may be supposed that, when the intermolecular cohesion is small in a cybotactic group and does not differ much from that among free water molecules, the average distance between the neighbouring molecules and consequently the specific volume of water will be nearly the same in the two cases. Consequently, the specific volume and the specific heat of the idealized liquid water will be those of the mixture composed of the free molecules and the cybotactic groups of weaker intermolecular cohesion, obtained by eliminating the effect of the cybotactic ice-crystals as was stated before.

### **Glassy State or Amorphous Solid**

It was commonly considered that the glasses are amorphous or super-cooled liquids. Recent investigation on amorphous solids of many substances<sup>1)</sup> with X-ray diffraction, has revealed the fact of an orderly arrangement of constituent atoms or molecules similar to that observed in the crystal of the same substance. The diffraction halo due to an amorphous solid is diffuse and broad. In this respect the amorphous solid resembles the liquid. On the other hand the position of the intensity maxima of the diffraction halo of an amorphous solid, coincides with that of the centre of average intensity of sharp and prominent diffraction lines due to the assemblage of an immense number of powdered crystals of the same substance, suggesting that the so called amorphous solid is composed of very small, submicroscopic crystals of the same substance. This suggestion seems to be half correct, but not entirely; because a considerable difference in density between the amorphous solid state and the crystalline state of the same substance is detected in many cases, being mostly smaller in the former state. Ordinarily, the word "amorphous" implies a random distribution of the constituent molecules. Thus the two ideas regarding the glassy state as amorphous and as crystalline are in themselves

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1. See for example; Randall: *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquid and Gases* (1934).

self-contradictory in the ordinary sense. However if we extend the writer's theory of the internal constitution of a super-cooled liquid to the temperature range very far below the freezing point of the substance, this self contradiction is completely reconciled. As is stated before, a super-cooled liquid of a substance is composed of two constituents: the free molecules and the cybotactic crystals. As to the relative amounts of these two constituents, the latter increases with decreasing temperature. When the temperature is so decreased as to be lower than the freezing point of the cybotactic crystals, the chance or probability of their spontaneous formation and of their growth becomes greater than the chance or probability of their decomposition into free molecules. Thus in this state, the major part of the constituent molecules will be united in the cybotactic crystals, leaving a minor

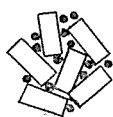


Fig. 6

part as free molecules; as is schematically represented by Fig. 6. The stability or the probability for persistence of an individual cybotactic crystal is of course very good in this case; but it is not absolute, and on the average a small degree of transformation from the cybotactic state to that of free molecules or vice versa is to be considered

to be going on from time to time. However, the relative proportion of the total amounts of the cybotactic crystals and the free molecules is a statistical problem, and is determined by the temperature. This is very different from the case of adult crystals, and is the reason that the amorphous solid has no sharp melting point. If this reasoning is correct, the amorphous solid or the solid in glassy state is simply a super-cooled liquid at a temperature, usually the room temperature, which is lower than the melting point of the cybotactic crystals. The resemblance of the x-ray diffraction halo caused by an amorphous solid of a substance to that caused by the powdered crystals of the same substance is now explained, if we consider that the halo is mainly due to the cybotactic crystals, which are the main composition of the amorphous solid and are supposed to consist mostly of cybotactic crystals having a size larger than the unit cell of the crystal of the substance at such a temperature. The cybotactic crystals or the groups are formed spontaneously here and there in the liquid. Thus when the larger part of the liquid is occupied by the cybotactic crystals, the remaining molecules, which can not occupy the lattice points, will be left and confined irregularly among the narrow and irregular interstices between neighbouring cybotactic crystals. This

seems to explain the remarkable difference between the densities of the amorphous solid of a substance and its crystal.

If the internal structure of an amorphous solid is like that sketched above at room temperature, then the melting point of the constituent cybotactic crystals will be much higher than the room temperature, and the growth of some of the cybotactic crystals may of course be possible by taking in neighbouring free molecules. But the cybotactic crystals are too numerous and consequently too close together, and the number of the free molecules situated at the crystal surfaces is too scant for such growth actually to occur; and the crystal growth i. e. the devitrification of glassy state happens at higher temperature. This is entirely the same as in the case of a super-cooled liquid which is not solidified.

When an amorphous solid is not completely solidified and is somewhat soft at a certain temperature, we can easily deform it plastically by applying a proper force slowly and continuously, i. e. the solid has some fluidity. But at the same time, it is brittle or fragile for a sudden shock, and we can break or shatter it into pieces by applying a sudden impact of sufficient strength. In such a state of the amorphous solid the larger part of the body will be in the state of the cybotactic crystals, but the transformation from the cybotactic to the free molecules and vice versa will be going on in some degree throughout the whole portion of the solid, and mutual displacements between all neighbouring small portions of the solid may take place slowly if compelled under the application of a sufficiently gradual force, by virtue of the cybotactic transformation. When the impact applied is too sudden and strong, the solid will not have enough time to accomplish the necessary mutual displacements between neighbouring portions in it, by the mutual transformation between the two kinds of molecular aggregation, i. e. the cybotactic crystals and the free molecules; and thus it is fragile under the sudden impact.

#### Beilby Layer on Polished Metal Surface

Beilby's hypothesis that the well polished surface of a metal consists of an amorphous layer has recently been tested by many authors by means of the electron diffraction. From the presence of the diffuse and broad halo, characteristic of the liquid, some have thought that they confirmed the correctness of the Beilby hypothesis. On the other hand, it may be imagined, from the approximate coincidence of



the position of the intensity maxima of the diffraction halo with that of the prominent diffraction lines due to powdered crystals of the metal, that the polished surface layer consists of very small metal crystals having a size not very much larger than that of the unit cell of the crystal. This point is not yet clarified, but it seems to be solvable by applying to this case the writer's idea of the internal structure of the solidified state of a super-cooled liquid. The main difficulty in doing this is that the melting of the surface layer by the process of abrasion and polishing should occur before solidification. But this will be easily overcome if we consider that the metal crystals at the surface are distorted and are smashed into very fine crystals having the size of the order of the unit cell of the crystal by the abrasion and the subsequent fine polishing, and consequently their melting point decreases enormously as was estimated in the case of the cybotactic ice-crystals. If so, local heating by subsequent polishing to a temperature above the so-decreased melting point may easily melt the fine crystals; and the solidified state of the super-cooled liquid of the metal may be produced by very rapid cooling occurring actually at the same time as the local heating. The fact that the electron diffraction halo obtained with a very finely polished metal surface indicates the presence of a half amorphous and half crystalline state, seems thus clearly explained, in accord with the writer's theory, by considering the formation of a solidified state of super-cooled liquid at the surface of the metal during the process of fine polishing.

The diffraction halo observed with the amorphous solid or the Beilby layer of a substance, corresponds, in main features, to the diffraction lines obtained with the powdered crystals of the same substance. But this correspondence is not exact. With a cybotactic crystal having the size of the order of the unit cell of the crystal, the atomic density in an atomic plane which reflects the x-rays or the electron wave is entirely different from that in the same atomic plane of an adult crystal, even in the case of the powdered ones which are enormously larger than a cybotactic crystal. As we are ignorant of the actual form of the cybotactic crystals, we can not enter into further details; but, at least, we must expect that some difference in relative intensities of the diffracted waves caused by various atomic planes will take place in both cases, i. e. with cybotactic crystals and with powdered crystals.

### Recrystallization of Cold Worked Metals

Lastly the writer will give some modification of the theory of recrystallization of a cold worked metal, which was proposed by the writer and Koyanagi<sup>1)</sup> several years ago. On that occasion it was assumed that the metal crystals melt more easily at their crystal boundaries, and when the lattice distortion is greater; and that the crystal nuclei, which are to grow to adult crystals by annealing, are formed spontaneously in the part thus melted by annealing at the crystal boundaries. To these assumptions the writer will add one more: i. e. the finer the crystals the lower their melting point as was assumed before. By cold working the metal crystals at different and numerous localities in the metal will be smashed into very fine crystals, even to the size of the order of the cybotactic crystals; and at the same time most of the fine crystals formed by smashing will be distorted to some extent. By being severely heated at various localities in the metal by subsequent cold working some of the very fine and distorted crystals at these localities will even be melted and cooled very rapidly by virtue of their remarkable low melting point, so that these portions come to the solidified state of the super-cooled liquid, whose internal constitution will be such as was pictured before by the writer. These localities in the solidified state of the super-cooled liquid have no definite melting point, and may also be said to be in the state of amorphous solid or in the glassy state in the sense the writer has previously indicated. When the metal in this state is annealed at a proper temperature these localities in the state of amorphous solid will be softened, and at the same time the other localities consisting of very fine crystals will be melted; and some crystal nuclei will be formed there. By continued annealing these nuclei will grow gradually in the softened part, and at the same time these softened amorphous parts will proceed further and further by consuming the remaining distorted fine crystals or the other softened amorphous parts. This is an outline of the writer's idea of the recrystallization of cold worked metals.

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1) U. Yoshida and K. Koyanagi: *These Memoirs*, A, 18, 9 (1935)