

## ON THE "TRIPLE MELTING" OF TRIPALMITIN

BY

Tsuneo SETO\*, Kenjiro ASAI\* and Akira MITO\*\*

(Received March 20, 1956)

### ABSTRACT

The mechanism of the "triple melting" was investigated on tripalmitin. Thermal and dielectric measurements, structure analysis by X-ray and electron diffraction methods, and microscopic observation were done for all polymorphic forms. The temperature dependency of these physical properties was examined and the behaviour of the phase transformation was observed. Some information on the stability of each phase was obtained.

The discussion on the mechanism of "triple melting" was made considering many experimental results.

### 1. Introduction

Triglycerides have at least three polymorphic forms. The three solid modifications have their respective melting points and there are no definite transition points among them, namely, the modification having the highest melting point is stable at all temperatures below its melting point, while the other two modifications can be obtained only as metastable phases. At temperatures below the lowest melting point any one of these three modifications can occur according to the cooling velocity from the melt, but crystallization from a solution always produces the stable modification. The so-called "multiple melting" is often observed when a sample settled in one of the metastable phases is heated at a proper velocity. According to Clarkson and Malkin (1), all the even and odd members of the homologous series from tricaprin to tristearin exhibit the polymorphism of this type. Since such behaviour is characteristic to triglycerides, it may be considered that it is due to the complicated shape of the triglyceride molecule which consists of three branches and is not linear.

Interesting properties of these substances as dielectrics which suggest the flexibility of the links between the alkyl groups and glycerol group have also been reported (2). Our work was attempted to understand the character of the triple melting, and polymorphism of tripalmitin was further studied by means of thermal analysis, dielectric measurement, microscopic observation, electron diffraction and X-ray diffraction. For

---

\* Physical Institute

\*\* Chemical Institute

the convenience of facilitating thermal treatment, tripalmitin was chosen for our experiments.

## 2. Experimental results

Tripalmitin used was prepared by reaction of purified glycerol (b.p. 169~170°C/15 mm. D<sup>14</sup>·1.264) and purified palmitic acid (m.p. 60.4°C) following C. Kailan and R. Obogi's direction (3). It was purified by successive recrystallization from purified ethyl alcohol and pure toluene and dried in desiccator under a reduced pressure. Its melting point was 65.5°C.

To begin with, the melting points of the metastable forms were examined by thermal analysis. When the metastable form was studied, heating and cooling had to be suitably quickened because of their tendency to change into more stable form. Therefore the size of the sample had to be small in order that the uniformity of temperature within the sample might be maintained during the observation. So, a small drop of the molten substance less than 1 mg in weight was put on the junction of the thermocouple which was made of fine wires of copper and constantan 0.01~0.05 mm in diameter, and was fixed as shown in Fig. 1. Measurements were done within the temperature range between 0°C and 80°C. Fig. 2 shows two typical curves with

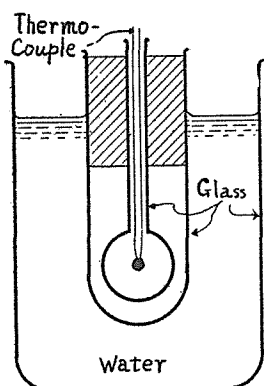


Fig. 1. A diagram for the thermal analysis.

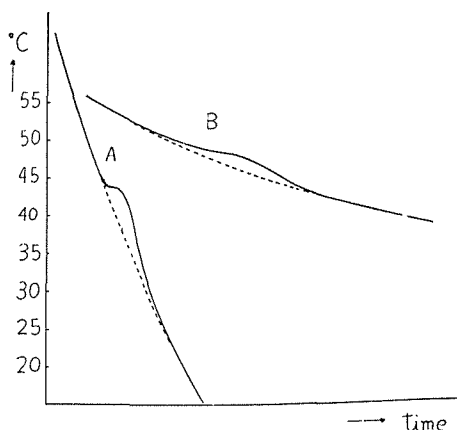


Fig. 2. Cooling curves  
(A) Rapid cooling, (B) Slow cooling.

different cooling rates. The curve for rapid cooling has a hump or a peak the top of which is lower than 44°C. If the cooling is handled more slowly, the temperature at which the anomaly in cooling curve occurs, shifts upwards and at the same time its shape becomes flat as represented by curve B. The samples solidified through these processes are semi-transparent.

The heating curves A and B in Fig. 3 were obtained for the samples which had

been subjected to rapid and slow cooling respectively from the melt and they may be regarded as the continuations from corresponding ones in Fig. 2. Curve A shows small heat absorption at about 65°C. Along curve B the heat absorption occurs twice at

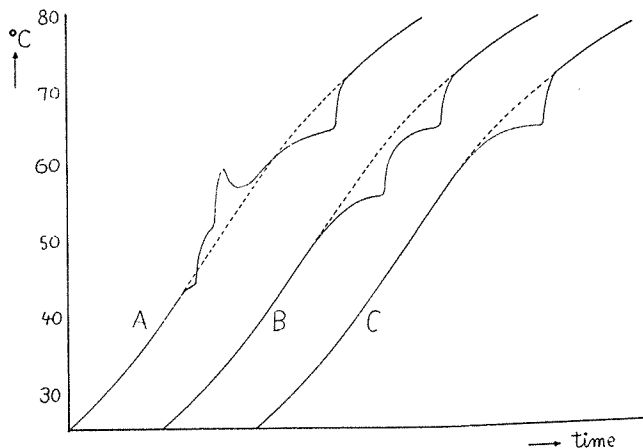


Fig. 3. Heating curves

- (A) For the rapidly cooled sample,
- (B) For the slowly cooled sample,
- (C) For the sample cooled very slowly from the melt, or kept at the elevated temperatures after solidification.

about 56.5°C and 65°C. If the drop has been cooled too slowly, the sample becomes opaque. For such sample, the heat absorption was observed only once (curve C).

According to the results of microscopic and electron diffraction studies the heat absorptions at about 44°C, 56.5°C and 65°C are due to the melting of three modifications and we shall call them respectively  $\alpha$  form,  $\beta'$  form and  $\beta$  form after Lutton (5). Figs. 2 and 3 show that the three forms can be realized by rapid, slow and extremely slow cooling respectively. The heat evolution peak on the heating curve A may be explained as follows: the first step corresponds to the heat evolution due to the crystallization of  $\beta'$  phase in the melt of  $\alpha$  and this increase in temperature of the sample induces further transformation of  $\beta'$  into the most stable  $\beta$  phase. The heat of transition is responsible for the second step of the peak. The temperature at the top of the first step is considerably lower than the  $\beta'$  melting point (56.5°C) and varies according to the mass of the sample, so the separation of the steps is not necessarily caused by the melting of  $\beta'$  phase.

The modifications appeared in the heating processes were identified by electron diffraction method. To observe the change in the transmission pattern, the specimen spread on the gold-leaf was heated in the diffraction apparatus, and three typical processes were observed according to the previous heat treatment. Starting with  $\alpha$

form, as increasing temperature, the liquid pattern instantaneously appears at about 44°C, and then  $\beta'$  and  $\beta$  patterns appear successively, the last one remaining until 65°C. The pattern observed at the time of  $\beta'$ - $\beta$  transition differed from either of  $\beta'$  and  $\beta$ , but it is uncertain whether this intermediate state is another modification or only a mixture of these forms. If the initial state is  $\beta'$  form, the pattern remains unchanged until the liquid is observed at 56°C. The  $\beta$  pattern never changes below 65°C.

Next, the change in dielectric constant associated with the phase transformation was studied by the tuning method. The results were consistent with those from the thermal analysis, although details could not be detected on account of large heat capacity of the condenser plates compared with the substance between them. Fig. 4 shows the behaviour of the dielectric constant  $\epsilon$  when the melt is rapidly cooled and then heated. The value of  $\epsilon$  increases with increasing temperature below the  $\alpha$ -melting point. This may be related to the orientational freedom of polar segments which has been suggested by Crowe and Smyth (2). In Fig. 5, when the melt is cooled down to about 50°C and is kept at this temperature,  $\epsilon$  begins to decrease and tends to the value for  $\beta$  phase. If the specimen is heated again before  $\epsilon$  could reach the final value, a peak is observed at  $\beta'$ -

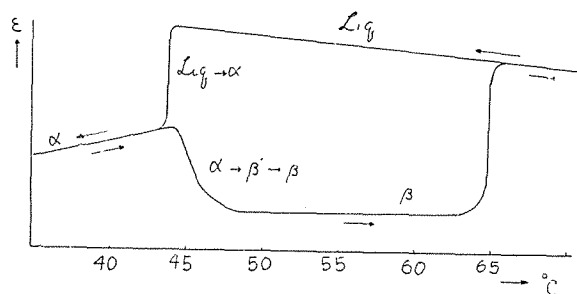


Fig. 4.  $\epsilon$ -temperature diagram for rapid cooling and subsequent heating.

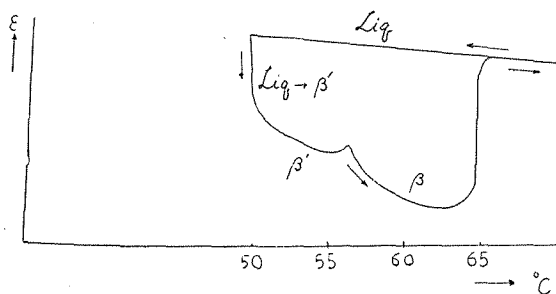


Fig. 5. Cooling was stopped at 50°C and the temperature was kept constant for 30 minutes and then heated. The curve shows some increase in  $\epsilon$  due to  $\beta'$  melting.

melting point, suggesting the melting of  $\beta'$  followed by the crystallization of  $\beta$  form. The temperature dependency of  $\epsilon$  of  $\beta'$  form could not be observed, because this phase is so changeable that it is scarcely isolated from other phases. Microscopic observation gave some results about the stability of  $\beta'$  phase. Fig. 6 shows the formation of  $\beta$  phase by very slow cooling at the temperature above the melting point of  $\alpha$ , and the poor temperature dependency of  $\epsilon$  was observed for this phase suggesting the lack of the dipole rotation because of the complicated crystal structure. These three curves, i.e. Figs. 4, 5, 6,

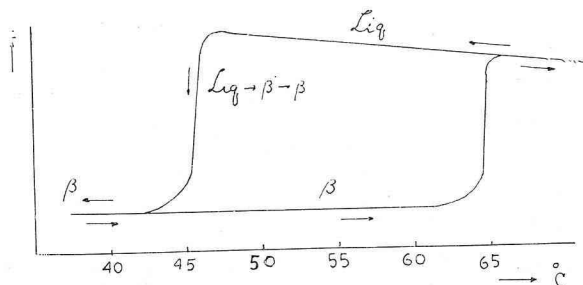


Fig. 6. On slow cooling,  $\epsilon$  began to decrease remarkably at 46°C due to the growth of  $\beta'$  form, but it then transformed to  $\beta$  form at this temperature and on heating  $\epsilon$  did not show any sign of the existence of the metastable phases.

correspond to the curves A, B, C in Fig. 3 respectively.

Plate 1 represents the cross nicol pattern of  $\alpha$  phase formed between two glass plates. If the solidification occurs at a temperature just below  $\alpha$  melting point,  $\alpha$  form makes spherulites, but only irregular aggregates are produced by too rapid cooling. When the temperature of

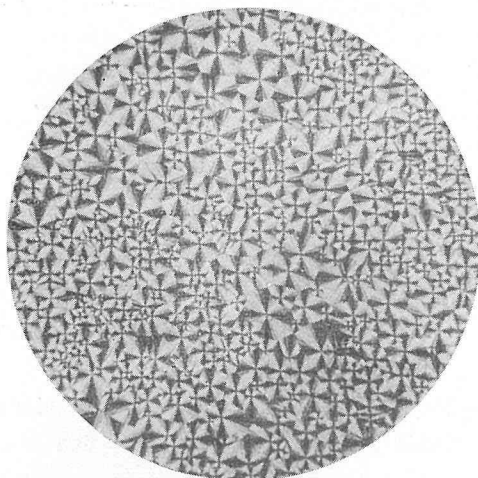


Plate 1.

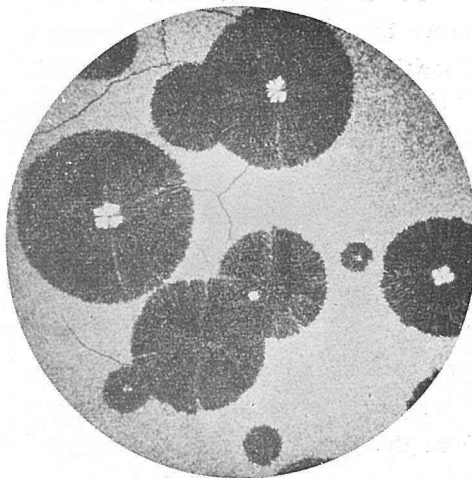


Plate 2.

undercooled liquid is kept between two melting points of  $\alpha$  and  $\beta'$  forms, spherulites of  $\beta'$  form grow. Plate 2 represents  $\beta'$  phase formed in a thin layer at 52°C. The back-ground is  $\alpha$  phase formed by subsequent chilling. In this temperature range both the rate of growth and the rate of nucleation of  $\beta'$  phase increase with decreasing temperature. In Fig. 7, curve A is a plot of the rates of increase in diameter of the spherulite as a function of temperature. The slope of the curve varies remarkably at about 46°C. But it was observed that the growth of the spherulite is caused by the growth of individual crystals at higher temperatures and by the formation of new crystals of its surface at low temperatures. Accordingly the high-temperature part of this curve represents the growth rate of the single crystal in the most rapid direction. On the other hand, the large rate at lower temperature may be attributed to some factors. These two types of  $\beta'$  form differ not only in size of the crystals but also in

melting point, the high-temperature type being more stable. Nevertheless no striking difference was found between them in the X-ray diffraction pattern except in diffuseness of the lines, and so both were treated as  $\beta'$  form. During the growth of  $\beta'$  phase,  $\beta'$  to  $\beta$  transformation proceeds, too. In Plate 2, the white spots near the centre of each circle represent those parts which have already transformed to  $\beta$  form. The growth rate of  $\beta$  crystal in this transformation is also shown by curve B in Fig. 7. Above the  $\beta'$  melting point,  $\beta$  phase grows only when it already exists in the melt, but spontaneous nucleation often occurs in a quite different way. When the melt is under-

cooled below the  $\beta'$  melting point, a cloud of minute crystals originates and spreads out at a rate far greater than the growth rate of individual crystals. The crystallization is completed in a short time and  $\beta$  phase is produced. In this case, the rapidity of the crystallization seems to be caused by very frequent nucleation stimulated by the motion of the minute crystals.

At last, each modification was studied by X-ray diffraction. The spacings obtained from the powder photographs are given in Table 1. The diffraction lines due to  $\alpha$  form were more or less diffuse, while the pattern due to  $\beta$  form was very complicated and the values of the spacing are not exact. For example, the strongest line could be separated into two lines of nearly equal intensity by rotating crystal method. Disregarding such details, the three modifications are characterized respectively by one, two and three strong diffraction lines. Clearly they correspond to the possible three modes of side packing of the long chains of the molecule, namely, hexagonal type, orthorhombic or monoclinic type and triclinic type respectively. Of course these types are common to aliphatic long chain compounds. If glycerol groups and other details are disregarded, it is possible to construct the crude models of the three forms after the examples of single chain compounds. In Fig. 8 the unit cells of such models are represented in cross-sections. The cross-section per hydrocarbon chain amounts to about  $19.8\text{\AA}^2$ ,  $19.2\text{\AA}^2$  and  $19.1\text{\AA}^2$  for the three forms respectively. Considering that the molecule of triglyceride consists of three chains, the true unit cells of  $\beta$  and  $\beta'$

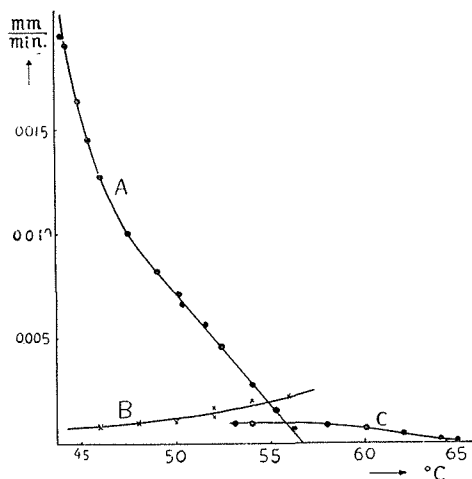


Fig. 7. The growth rate of the crystal  
(A)  $\beta'$  spherulite in the liquid phase,  
(B)  $\beta$  crystal in  $\beta'$  phase,  
(C)  $\beta$  crystal in the liquid phase.

Table 1.

$\alpha$ form (vertical)		$\beta'$ form (tilted)		$\beta$ form (tilted)	
45.2	v. s.	42.0	v. s.	40.3	v. s.
15.2	s.	13.8	s.	13.45	s.
9.06	w.	8.5	w.		
7.59	w.	7.05	w.	6.70	w.
5.70	w.	5.37	w.	5.03	w.
4.15	v. s.	4.21	v. s.	4.56	v. s.
2.39	w.	3.78	s.	3.84	s.
2.10	v. w.	3.07	m.	3.68	s.
		2.79	w.	3.41	m.
		2.54	m.	2.56	s.
		2.25	m.	2.35	m.
		2.07	w.	2.26	m.
		1.88	w.	2.18	m.
		1.77	m.	2.12	m.
				2.06	m.
				1.95	m.

forms must have areas at least  $3/2$  times as large as the corresponding units in Fig. 8. Vand and Bell (4) obtained more detailed figure on the crystal structure of  $\beta$  form of trilaurine. In  $\alpha$  phase, however, it is possible to construct

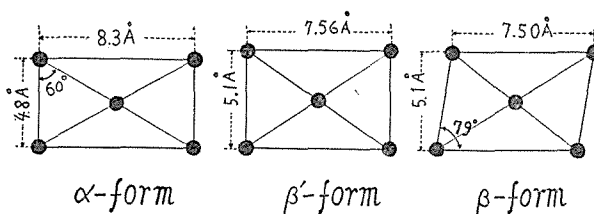


Fig. 8. Cross-sections of the units of three forms which correspond to the unit cells of paraffins.

one molecule with any three neighbouring chains on account of the high symmetry of the crystal. So any conclusion on the regularity of the arrangement of the glycerol groups in  $\alpha$  phase, is difficult to deduce.

### 3. Discussion

The symmetry of  $\alpha$  form may be described as being hexagonal. In general, such symmetry of vertical forms is associated with the rotational freedom of the linear chain molecules around their long axes. But triglyceride molecules are not linear. Clarkson and Malkin (1) concluded from their X-ray investigation for long spacings the shape of the triglyceride molecule to be like a tuning fork. The three chains in a molecule are joined to the glycerol group with C-O-C bonds. If the bonds were sufficiently flexible, the individual chains would be allowed to rotate in  $\alpha$  phase, just

as the linear molecules in the high-temperature modifications of hydrocarbons. But the triglyceride molecule is composed of three chains connected to the glycerol group, so the rotation of the individual chain does not necessarily bring the hexagonal symmetry of the crystal structure as in the case of the linear chain molecule. It is rather reasonable to think that the hexagonal symmetry of  $\alpha$  phase is due to the disordered arrangement of the molecules inherited from the liquid phase, so in this case the rotational motion of individual chain is not the necessary condition for the hexagonal symmetry. The fact that no marked phase transformation to non-rotating ordered state occurs by further cooling, which is usually observed for the molecular rotating phase of the linear chain molecule, seems to support this view point.

For  $\beta'$  form, which is monoclinic or at least nearly monoclinic, the chains are considered to be most commonly arranged. Such configuration of the chains will require the regular arrangement of molecules. But since the cross-section of the chain (about  $19.2\text{\AA}^2$ ) is somewhat larger than usual (about  $18.5\text{\AA}^2$ ), some degree of orientational freedom of the chains around their axes may occur.

$\beta$  form is clearly triclinic and is most peculiar modification, though a few examples of other long chain compounds have similar structures.

Fig. 9 represents the schematic process of the triple melting. The liquid phase can be easily undercooled until the solid modification of highest entropy  $\alpha$  grows. This phase remains unchanged provided the temperature is sufficiently low. On heating such sample settled in  $\alpha$  phase, it once melts at its melting point (A), leaving seeds of  $\beta'$  form as seen from the microscopic observation. They soon grow up into  $\beta'$  phase. On further heating, it changes again to  $\beta$  phase in the same manner at the  $\beta'$  melting point (B). The last phase melts at the highest melting point (C). Actually this process must be disturbed by the transformation between solid phases.

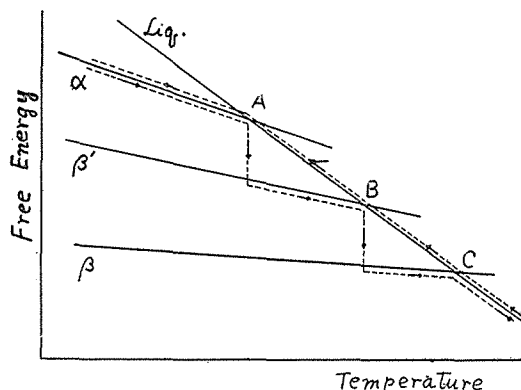


Fig. 9. Free energy *versus* temperature diagram for the liquid and three solid phases. Dotted line shows the triple melting process.

For most aliphatic long chain compounds the relative stability of polymorphic forms at the melting point is delicate, while that of triglyceride shows the distinct tendency that the form with higher symmetry is less stable. So far as the arrangement of the chains is discussed, the crystal structure of each modification of tripalmitin compared



with other long chain compounds has not particularity to be specially mentioned. The long chain parts of triglyceride are forced to be packed in a manner similar to that for single chain molecules, the presence of glycerol links combining each one of three chains resists to this tendency and will cause the deformation of the molecules from their stable configuration and will limit the freedom of the chains, that is, the linkage will tend to raise the free energy of the modification relative to that which would be expected for linear chains. This effect of the linkage on the stability may be large for the high-symmetry form, the structure of which is favourable to free chains, but the effect must be minimized for low-symmetry form where the molecules are fixed in the most stable positions. Consequently the free energy of high-symmetry phase may be raised relative to that of the low-symmetry phase. If this effect is comparable to that for liquid phase, the high-symmetry phase will lose its stable region.

From the standpoint of phase transformation, the shape of the molecule is evidently favourable to disordered phase, because the probability that molecules are placed in order is very small even if the chain parts of them are almost regularly arranged. If  $\alpha$  form permits irregularity in the orientation of the molecules, the growth of this phase may be accomplished without interchange in the position of neighbouring chains, since the chains are expected to be nearly parallel to each other in supercooled liquid. While the molecules are regularly arranged in  $\beta$  phase and perhaps in  $\beta'$  phase, so the rates of nucleation and growth of these phases must depend on the symmetry and the shape of the molecule. At lower temperatures, the mobility of the molecules become important, because the rotation of the molecule which is necessary for the growth of ordered phase will require the interchange of the position of neighbouring chains. This means that the growth of the disordered phase becomes dominant with decreasing temperature.

The phase transformation between solid phases will be accompanied by another difficulty which arises from the difference in tilt angle. In fact, the slowness of such transformation has been observed even in single chain substances such as higher alcohols. In triglyceride, in addition to the above-mentioned difficulty the glycerol rinks may be responsible for the occurrence of the metastable phases.

Besides the phenomenon of multiple melting, tripalmitin has another peculiarity in polymorphism. Solid samples exhibit different properties depending on the difference in the temperature at which they have grown, even if they assume the same polymorphic form.  $\beta$  phase which has transformed from  $\beta'$  phase, melts at a temperature lower than the true melting point observed on that which has grown slowly from the melt. Lutton (5) found that the melting point of  $\beta$  phase just formed can be raised by keeping its temperature near the melting point. The melting point and the sharpness of the X-ray diffraction lines of  $\beta'$  form increase with the temperature at which

this phase has grown. Probably the distinction between high- and low-temperature types of this form is not so essential. The melting point of  $\alpha$  phase could not be measured accurately on account of the rapid transformation to more stable forms near the melting point, but the breadth of diffraction lines shows the same tendency as  $\beta'$  form.

These facts suggest the presence of the lattice imperfections. When the crystal grows at lower temperatures, the faults at which some molecules are fixed in wrong orientation will occur more frequently than at higher temperatures. Such imperfection will cause the decrease in melting point, since the imperfection may be expected to last until the temperature approaches the melting point.

#### Acknowledgement

In conclusion, the authors wish to express their thanks to Prof. K. Tanaka and Prof. R. Goto for their helpful discussions and advices. This work has been carried out by a grant-in-aid of the Ministry of Education.

#### REFERENCES

1. C. E. CLARKSON and T. MALKIN: J. Chem. Soc. (1934) 665; (1948) 985.
2. R. W. CROWE and C. P. SMYTH: J. A. C. S. 72 (1950) 5281.
3. C. KAILAN and R. OBOGI: Monatsheft für Chemie 45 (1925) 215.
4. V. VAND and I. P. BELL: Acta Cryst. 4 (1951) 465.
5. E. S. LUTTON: J. A. C. S. 67 (1945) 524.