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High-temperature X-ray diffraction: experience in the use of samples on a backing plate for studying crystalline phases mixed with the liquid

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ABSTRACT. This review covers the operating procedures for X-ray diffraction studies of materials and processes in the presence of the liquid phase over a wide range of temperatures using standard X-ray diffractometers with a polycrystalline sample on a backing plate. The feasibility of using high-temperature X-ray diffraction to study materials during melting and crystallisation, to construct the supersolidus parts of equilibrium diagrams of systems, to investigate fluid crystalline materials, to find the optimum conditions for preparing materials from a solution in the melt, etc. is demonstrated.

The bibliography comprises 14 references.

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I. Introduction

High-temperature X-ray diffraction has in recent decades been used successfully to study crystalline materials at different temperatures. The method has been used to determine the phase composition of a material, its crystal structure, and thermal expansion and to study high-temperature solid state transitions. Results obtained from high-temperature X-ray diffraction studies are used to construct the subsolidus parts of equilibrium diagrams of systems and as a check on the creation of technologies and materials which will function at high temperatures.[1–5]

High-temperature X-ray diffraction can also be used to study samples in the presence of a liquid.[6,7] However this facility is not often used and the results available are therefore not very complete. A choice has to be made between the two main methods of preparing a sample for investigation: packing the powder into a holder or applying the powder to a backing plate. These methods are equally laborious and similar in cost but the second fundamentally expands the potentialities of the method because it enables the material to be examined not only as a solid but also as a mixture of solid and liquid, e.g. during melting of a crystalline material.

The aim of this paper is to review and popularise the practice of using samples on a backing plate for high-temperature X-ray diffraction studies.

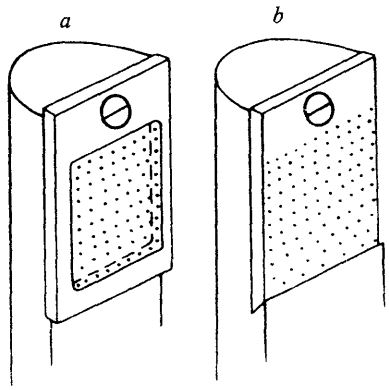


Figure 1. Powder samples for high-temperature X-ray diffraction prepared: *a*, in a holder; *b*, on the surface of a plate.

II. The sample for high-temperature X-ray diffraction

The powdered compound under investigation is usually packed into a holder made of a chemically inert material (Fig. 1*a*). Due to the geometry of the diffractometer the holder is positioned vertically and consequently on heating the material may crumble and slip down and on fusion it may run out of the holder. A more reliable specimen is obtained by depositing a thin layer of the powder on a thick plate, a backing plate,[5–7] which is not the heater (Fig. 1*b*). When this type of sample is heated above the melting point of the compound under investigation the liquid almost always wets the vertical surface of the backing plate and remains on it. An inert material, e.g. platinum, is used for the backing plate.

If the thermal expansion coefficient of the backing plate is known the latter can be used as an "internal" standard by measuring the reflection angles at all the temperatures studied. The risk of the specimen and the standard contaminating each other on heating is then less than when a powdered internal standard is used.

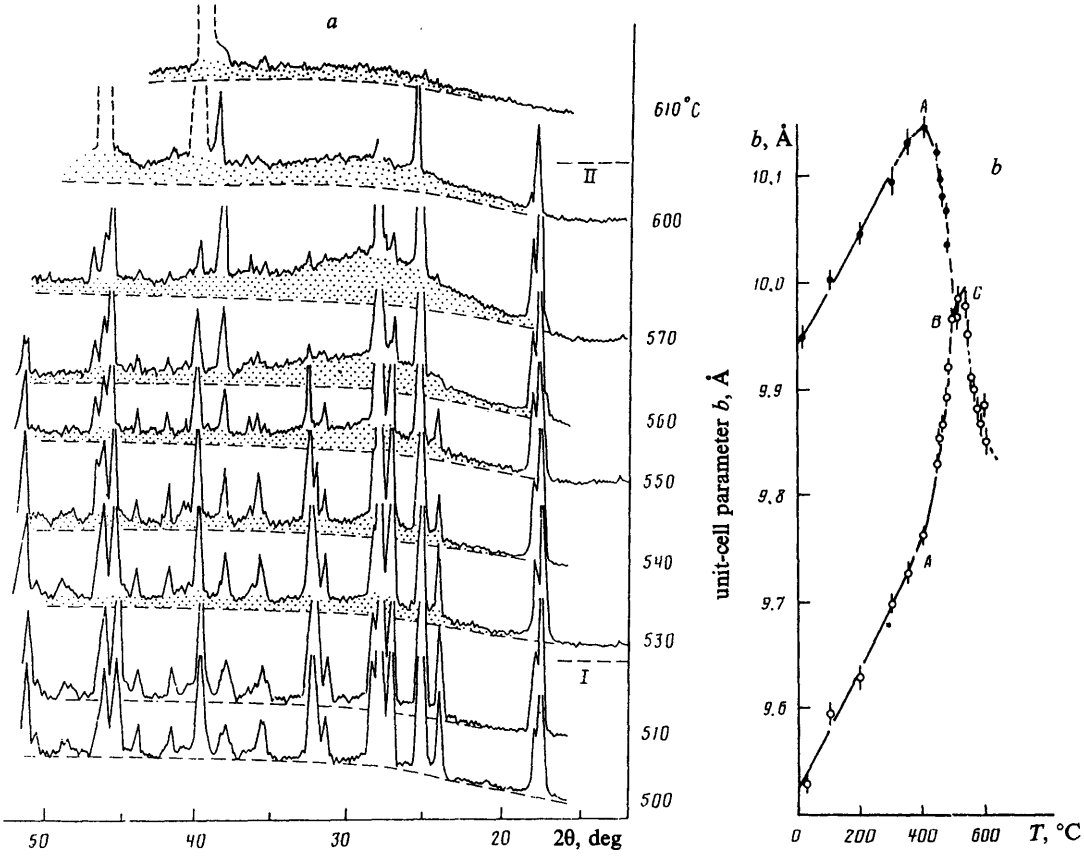


Figure 2. Typical changes with temperature in the X-ray diffraction pattern (*a*) and the unit-cell parameter (*b*) of solid solutions. Specimen composition: 80 mol% $NaVO_3$ + 20 mol% KVO_3, monoclinic phases, diopside structure type; CoK_α radiation.

A uniform thin layer (0.2–0.4 mm) of the powder on the backing plate can be obtained as follows. The plate is laid horizontally, a small quantity of the powder (some tens of milligrams) poured on to it, a few drops of alcohol added, the material levelled out with a thin (ø ≈ 0.1 mm) steel wire and kept in suspension for several minutes until all the alcohol has evaporated. If the material reacts with alcohol or the water present in it another highly volatile liquid must be used.

The thickness chosen for the layer of powder is such that the diffraction peaks from the backing plate (platinum) are completely absorbed. For inorganic compounds a layer of powder 0.2–0.4 mm thick satisfies this condition. However if the peaks from the backing plate are to be used as internal standards a thinner layer of powder is applied.

A very small amount of material is required for this type of sample, the specimen is stable at different temperatures, and solid and liquid phases can be studied concurrently.[5–13]

The representative costs of the labour and materials involved in preparing such a sample are nothing compared with the difficulties of setting up an X-ray diffractometer with a horizontal sample surface because with a geometry of that type the counter would have to rotate in a vertical plane.

III. Studies of the fusion of materials

Determinations using the halo due to the amorphous phase. Using X-ray diffraction, melting is defined by the disappearance of the diffraction maxima belonging to the crystalline phase and the appearance of a halo due to an amorphous phase (see, for example, Fig. 2*a*, 610 °C).

Melting of part of the material may be indicated by the appearance of a halo and substantial changes in the relative intensities and positions of the diffraction maxima taking place due to recrystallisation of the solid phase in the melt with a change in its chemical composition and the possible emergence of texture; compare, for example, Fig. 2*a*, 510 °C (before melting) and 560 °C (after partial melting).

If some of the melt runs off the vertical surface of the specimen holder the diffraction peaks due to the backing plate material may appear or be intensified in the diffraction pattern (see broken lines in Fig. 2*a*, 600° and 610 °C).

For a sample from the $NaVO_3$–KVO_3 system (4:1) (Fig. 2*a*) melting as defined by the criterion described starts in the region of 530 °C (line *I*) and is complete at 605 °C (line *II*).

As the halo is normally detected when there is a sufficiently large amount of the melt, there is an appreciable threshold in the sensitivity of this method to the appearance of the melt (10%).

Determinations based on the lattice parameters. The variation of the crystal lattice parameters with temperature is often a more sensitive "indicator" of melting. The onset of melting is marked by pronounced changes in the relationship. For example, for the 4:1 specimen in the $NaVO_3-KVO_3$ system melting, as defined by this criterion, starts at 535 °C (point *C* in Fig. 2*b*) and is complete at 610 °C. The detection of melting from the changes in the unit-cell parameters *b*, β, and the unit-cell volume *V* give consistent results within a few degrees.

IV. Determination of the lattice parameters of crystalline phases in mixtures with the liquid

The unit-cell parameters of a crystalline phase mixed with the liquid can be determined using a sample on a backing plate. The first such determination was made in a study of the $NaVO_3-KVO_3$ system.[12] As an example, the temperature dependence of the unit-cell parameter *b* of a 4:1 specimen from this system is shown in Fig. 2*b*. The specimen consists of two monoclinic phases of the diopside type. When these are heated, up to a certain temperature (400 °C, point *A* in Fig. 2*b*) they undergo only thermal expansion but between points *A* and *B* (~400–500 °C) the phases are homogenised, then on the section *BC* (500–530 °C) the homogeneous solid solution undergoes thermal expansion, and at point *C* (530 °C) it starts to melt.[5]

V. Studies of the supersolidus parts of equilibrium diagrams

High-temperature X-ray diffraction is widely used together with thermal analysis to study the equilibrium diagrams of systems, mainly because it is advantageous for the interpretation of transitions and identification of the phases.

It is usually used to study the subsolidus part of an equilibrium diagram. When using the method in its standard version, the formation of a liquid phase makes further investigation impossible because the material runs off the vertical plane of the sample.

Using a sample on a backing plate enables not only the solid state transformations but also the solidus and liquidus lines to be studied, i.e. a complete high-temperature X-ray diffraction study of the equilibrium diagram of a system to be made.[5,10,12,13]

Solidus and liquidus lines (plotted at various compositions). The methods described above (see Section III) are used to determine the temperatures of the commencement and termination of melting for specimens with different chemical compositions and then the solidus and liquidus lines are plotted.

Solidus line (plotted at a single composition). This is achieved using the unit-cell parameters of solid solutions. The variation of the unit-cell parameters with temperature and chemical composition is studied. The unit-cell parameters of the crystalline phases are measured at various temperatures. The dependence of these parameters on temperature and composition is used to calculate the chemical composition of the solid solutions at each temperature at which measurements are made. The points obtained are plotted on the equilibrium diagram and the interphase boundaries (solidus, binodal decomposition curve) are constructed from them.

The variation of the parameter *b* of the monoclinic solid solutions $K_xNa_{2-x}V_2O_6$ in the $NaVO_3-KVO_3$ system with temperature (*T*, °C) and potassium content (at.%) is described by the equation:

$$b = 9.478 + 0.55 \cdot 10^{-3} T + 0.0117x.$$

Part of the equilibrium diagram of the system, obtained by studying a specimen with an Na:K atomic ratio of 4:1, is shown in Fig. 3. When the temperature is raised above the solidus line this specimen breaks down into a liquid phase which is richer in potassium and a solid solution richer in sodium. In this case heating leads not only to the customary thermal expansion but also to a change in the chemical composition of the solid solution. Consequently, as is clear from Fig. 2*b*, on heating beyond point *C* the replacement of potassium ions by the smaller sodium ions leads to a marked contraction of the structure in spite of the thermal expansion that is taking place.

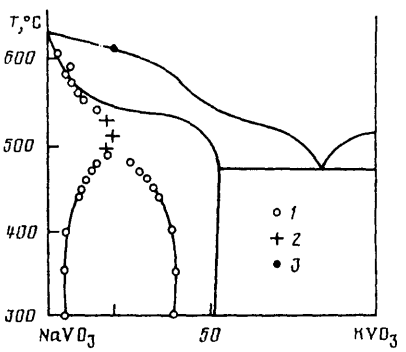


Figure 3. Construction of the equilibrium diagram of the $NaVO_3-KVO_3$ system. The experimental points were obtained using the parameter *b* for two-phase specimens (*1*) and single-phase specimens (*2*) and from the disappearance of peaks due to a crystalline phase (*3*).

The eutectic. Aspects of the X-ray diffraction study of melting in the region of the eutectic (475 °C, 83 mol% KVO_3) are illustrated in Fig. 4. When a specimen containing 80 mol% KVO_3 is heated, initially the peaks belonging to one phase (shown hatched in Fig. 4) disappear and a halo due to the liquid phase appears. There are no marked changes in the positions of the peaks belonging to the other phase or in its unit-cell parameters above the eutectic temperature (because there is no appreciable isomorphous miscibility) right up to the liquidus line, at which point these peaks disappear (*cf.* the melting of the solid solution, Fig. 2).

For compositions lying to the left of the eutectic, the diffraction peaks belonging to the right-hand phase disappear first and for those lying to the right of the eutectic, the peaks due to the left-hand phase disappear first. The composition of the eutectic is taken to be the mean between the two closest compositions at which different phases disappear. The melting point of the eutectic is the temperature at which one of the phases in the eutectic mixture

disappears. The closer the chemical composition of the specimen to that of the eutectic mixture the more melt is formed at the eutectic temperature (and hence the stronger the halo).

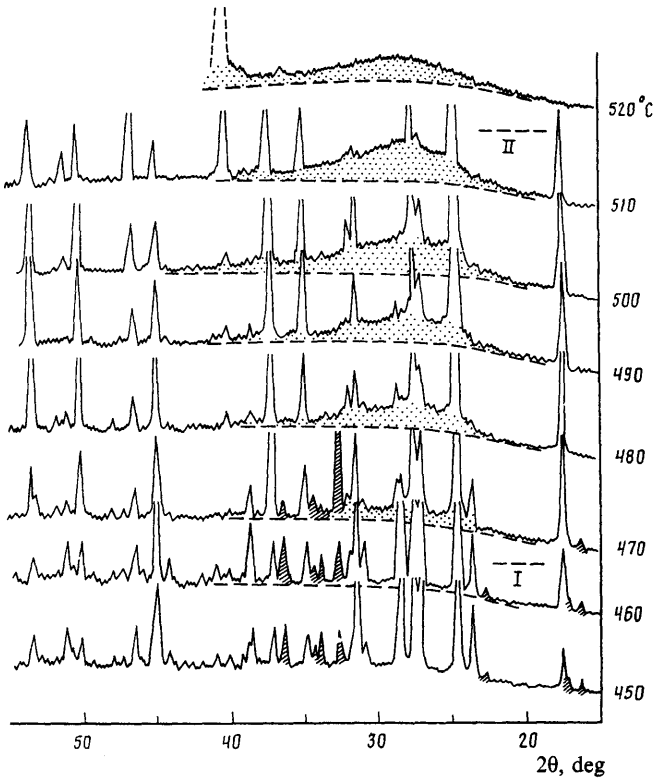


Figure 4. Typical changes in the X-ray diffraction pattern of a eutectic mixture with temperature. Specimen composition: 20 mol% $NaVO_3$ + 80 mol% KVO_3; the KVO_3 peaks are hatched and those due to $KNaV_2O_6$ are not; CoK_α radiation.

High-temperature X-ray diffraction gives some unexpected results in studies of the melting of eutectic systems. Note in particular that in the example we have been discussing (Fig. 4) the first phase disappears at a temperature (475 °C) which is 20° above (and hence later than) the appearance of the halo due to the liquid (455 °C), rather than simultaneously. Insufficiently studied premelting processes may be the cause of this.

High-temperature X-ray diffraction makes it possible to observe phases and processes at different temperatures directly and to identify them objectively. It is therefore advisable to use this method of studying equilibrium diagrams in conjunction with other methods of thermal investigation.

VI. Finding the optimum conditions for preparing materials

Reactions between substances are more rapid in the melt than between solid phases. For this reason it is helpful to introduce an easily fusible component into the mixture.

For example, in order to prepare anorthite $CaAl_2Si_2O_8$, $CaCl_2$ (m.p. 777 °C) was mixed with dickite $Al_2Si_2O_5(OH)_4$ in a 1:1 ratio, the mixture was heated, and X-ray diffraction patterns recorded at various temperatures (Fig. 5).[5] In the pattern recorded at 600 °C the diffraction peaks belonging to $CaCl_2$ are hatched. On reaching 700 °C the peaks belonging to dickite disappear due to dehydration and conversion to a metakaolinite that is amorphous to X-rays (thermographic and quenching data). The diffraction pattern recorded at 800 °C contains no peaks belonging to $CaCl_2$ either, indicating that the metakaolinite phase is in a $CaCl_2$ melt. This state also persists at 900 °C (Fig. 5).

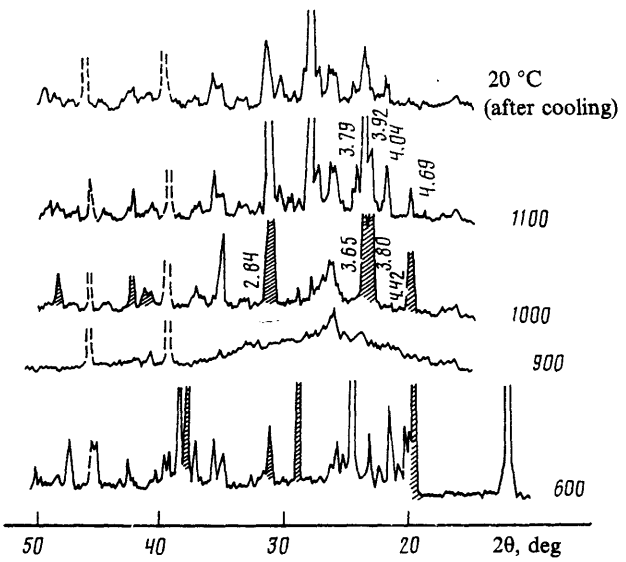


Figure 5. Preparation of anorthite: X-ray diffraction patterns of dickite mixed with $CaCl_2$ (the peaks at 600 °C due to the latter are hatched) and the products obtained by heating them (CuK_α radiation).

At 1000 °C a new structure (a layer type anorthite with the interplanar spacings d = 4.42, 3.80, 3.65, and 2.84 Å) is found in the products and when the temperature is raised to 1100 °C this is transformed to a framework modification of anorthite (with d = 4.69, 4.04, 3.92, and 3.79 Å) which is retained on cooling to room temperature.

In this experiment the film of liquid was kept on the vertical backing plate by surface adhesion forces (see Fig. 5, 900 °C). This permitted direct "observation" of the synthesis of anorthite involving the liquid phase, determination of the synthesis temperature, and the discovery that a layer-type modification of anorthite is formed initially (at 950 ± 50 °C) and is irreversibly converted to the more stable framework modification of this compound at 1050 ± 50 °C.

VII. High-temperature studies of fluid materials (taking rotational crystals — paraffins as an example)

Certain crystalline compounds display considerable fluidity, especially at temperatures near the melting point. High-temperature studies of fluid materials are not feasible on standard X-ray diffractometers with the sample packed into a vertical holder but no technical difficulties are encountered if the sample is placed on a backing plate.

Let us take as an example the normal paraffins C_nH_{2n+2}. At low temperatures these have normal crystal structures with three-dimensional periodicity but on heating they change, due to rotation of the linear molecules around their axes, to rotational crystals which have one-dimensional periodicity and finally melt, losing the periodicity. In all these states paraffins can be retained safely on the vertical surface of a sample for high-temperature X-ray diffraction.

The polymorphism of paraffins. The diffractometer traces in Fig. 6 show that the low-temperature orthorhombic modification of the paraffin with $n = 23$ changes at 40 °C to the (comparatively) high-temperature hexagonal rotational modification (the 200 and 110 peaks merge together) which melts at 47 °C. X-Ray diffraction studies of other members of the homologous series show that, contrary to the accepted opinion, the paraffins with n odd and less than 23 melt without reaching the hexagonal state.[11]

Ranges [of existence] of paraffin solid solutions. Both in nature (as concomitants of petroleum, coverings of plants) and in industries (packaging, food, electronic, and other branches) paraffins usually occur as a mixture of many homologues. For this reason studies have been made of the ranges of existence of solid solutions of different paraffins and the effect of the formation of solid solutions on polymorphism, melting, and other properties of paraffin compositions.[14]

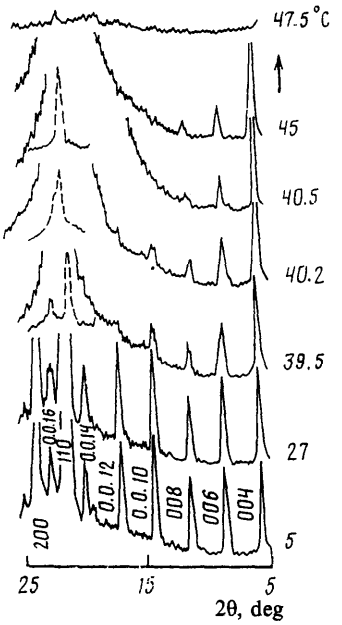


Figure 6. X-Ray diffraction patterns of the paraffin with $n = 23$ at different temperatures.[11] The peaks shown by broken lines were re-recorded using an anode current 10 times smaller; CuK_α radiation.

The data plotted in Fig. 7 show that when a homogeneous orthorhombic solid solution with the composition $C_{21}H_{44}:C_{23}H_{48} = 1:5$ is heated it breaks down at 30 °C to give two orthorhombic solid solutions, then at 34 °C the mixture of phases becomes homogeneous again, and close to 39 °C it changes to the hexagonal

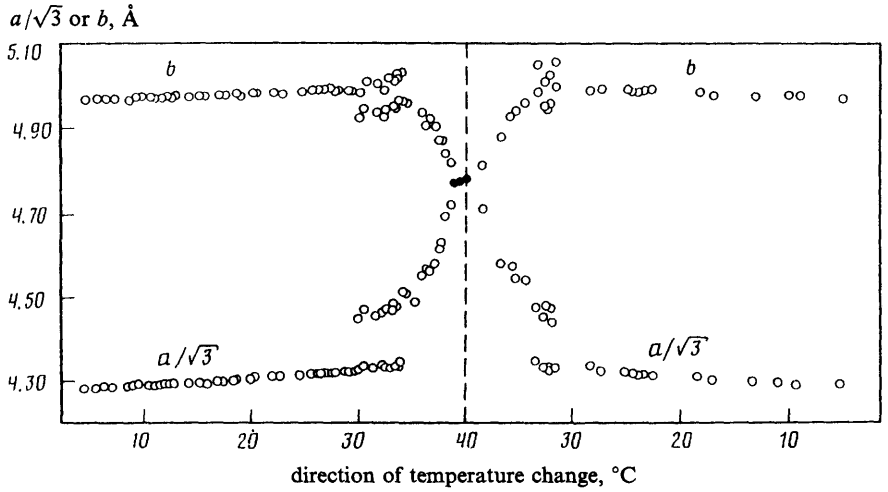


Figure 7. Variation with temperature (both heating and cooling) of the parameters $a/\sqrt{3}$ and b of the orthorhombic and hexagonal unit cells of a paraffin solid solution with the composition $C_{21}H_{44}:C_{23}H_{48} = 1:5$. The dark points relate to the hexagonal modification.

phase. On cooling these changes are repeated in the reverse sequence. This is the only example we know of where the range of the solid solution contracts on raising the temperature. It is evidently connected with the rotation of the molecules.

When the solid solution is heated the shorter aliphatic chains in the paraffin with $n = 21$ reach critical amplitudes of swinging, and possibly complete rotation around their axes, at an earlier stage and they escape from the structure of the homogeneous solid solution; at a temperature a few degrees higher when the longer molecules with $n = 23$ reach a comparable degree of oscillation or rotation, all the molecules again become comparable in energy and the mixture becomes homogeneous again.[14]

VIII. Conclusion

The high-temperature X-ray diffraction of polycrystalline samples is an objective method of studying the qualitative and quantitative phase composition of crystalline materials during a variety of solid-state thermal changes.

Using a standard X-ray diffractometer with a polycrystalline sample in the form of a thin layer of material on an inert backing plate also enables us to study crystalline materials in contact with the liquid phase, i.e. to study fusion, crystallisation, and recrystallisation processes. This provides opportunities for the complete high-temperature X-ray diffraction study of the equilibrium diagrams of systems, including their supersolidus part, and also for investigating the processes of the formation of crystalline materials from the liquid, and modelling magma and other processes involving the liquid phase.

The experience in the use of samples on a backing plate built up in the Department of Crystallography of St. Petersburg University over a period of twenty-five years shows that films of melts of various chemical compositions can be maintained on the vertical surface of a platinum backing plate by adhesion forces, so making it possible to carry out the high-temperature X-ray diffraction studies that have been described.

We can be confident that this experience will promote a wider application of high-temperature X-ray diffraction, especially with the use of a sample on a backing plate, for solving problems in crystal chemistry, physical chemistry, materials science, etc.

I am grateful to my colleagues, especially R S Bubnova and E N Kotel'nikova, for the joint research which I have quoted in this review.

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