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THE USE OF X-RAY POWDER DIFFRACTION FOR THE STUDY OF THE KINETICS OF PHASE TRANSITIONS

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The use of X-ray powder diffraction for the study of the kinetics of phase transitions.

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Abstract

A method is presented for the elucidation of the mechanisms of structural phase transitions and the determination of some thermodynamic parameters using time resolved powder diffraction. The method is illustrated with a study of the $I \leftrightarrow II$ phase transition of ammonium chloride using data collected at the energy-dispersive powder diffraction facility of the UK synchrotron radiation source (SRS).

1 Introduction

An investigation of the kinetics of a phase transition or chemical reaction begins by measuring the degree of transformation (α) from one phase to another, as a function of time, for various conditions of pressure, temperature and composition. These measured α curves are then compared with calculated curves in order to determine which kinetic model best describes the transformation. Important parameters such as the activation energy and the order of the transformation, and the equilibrium transition temperature or pressure can be determined once a suitable model has been found. Powder diffraction is especially useful for determining the degree of transformation since it yields information on all of the crystalline components of a system and can be used to study complex systems where a number of reactions may be occurring simultaneously [1, 2]

We here first outline the basic principles involved in a kinetic study and then illustrate the method with a study of the $I \leftrightarrow II$ phase transition of NH_4Cl . Although we describe the method in terms of varying temperature we could equally well have varied the pressure.

2 Choosing a suitable diffraction method

A standard powder diffractometer is unsuitable for kinetic studies: with the scanning $\theta/2\theta$ method peaks at different parts of the scan are measured at different stages in the reaction, and simply setting the detector at one 2θ angle where there is a strong reflection and monitoring the intensity of that peak as a function of time is also unsatisfactory since the positions of diffraction peaks often change due, for example, to thermal expansion, during a reaction or phase transition. The whole diffraction pattern must be collected simultaneously and as rapidly as possible. There are two diffraction geometries that may be used to study kinetics:

1. A monochromatic beam of X-rays and a position sensitive detector.
2. A polychromatic beam of X-rays and an energy-dispersive detector.

Although the energy-dispersive method suffers from a much lower momentum resolution than the monochromatic method it has the important advantage that the diffraction geometry can be optimised to exclude any scattering from the sample environment.

3 Determining the degree of transformation

For a solid state phase transformation the degree of transformation can be determined directly from the relative intensities of the peaks in the powder pattern. If phase A transforms into phase B then the degree of transformation at time t is given by:

$$\alpha_t = x_B(t) = 1 - x_A(t) \quad (1)$$

where $x_A(t)$ and $x_B(t)$ are the mass fractions of A and B respectively.

For a mixture of two phases A and B with mass absorption coefficients μ_A and μ_B the intensity of a reflection with miller indices (hkl) from phase A is given by [3]:

$$\frac{I_{A(hkl)}}{I_{A(hkl)}^\infty} = \frac{x_A \mu_A}{x_A(\mu_A - \mu_B) + \mu_B} \quad (2)$$

where $I_{A(hkl)}^\infty$ is the intensity of reflection (hkl) from phase A when only phase A is present. Combining these two equations and assuming that the mass absorption coefficient of the two phases is the same we get the following expression for the degree of transformation:

$$\alpha_t = \frac{I_{B(hkl)}(t)}{I_{B(hkl)}(\infty)} = 1 - \frac{I_{A(hkl)}(t)}{I_{A(hkl)}(0)} \quad (3)$$

So a kinetics study using powder diffraction involves collecting time resolved powder diffraction spectra from a system before, during and after a transformation or reaction and then using these spectra for quantitative analysis of the system. Only one

reflection of phase A or B needs to be monitored as a function of time in order to determine α although a number of reflections are usually monitored and their estimates of α combined.

4 Determining the equilibrium transition temperature

At constant pressure the change in the Gibbs free energy ΔG on going from phase A to phase B is related to the change in entropy ΔS by:

$$\Delta G = \Delta S(T - T_c) \quad (4)$$

where T_c is the thermodynamic equilibrium temperature of the transition and T is the current temperature. The two phases are in equilibrium at temperature T_c , above T_c phase B is more stable and below T_c phase A is more stable. If phase A is heated from T_1 to T_2 it transforms into phase B with a change in Gibbs free energy ΔG . The further T_2 is above T_c the faster the reaction proceeds. Due to inertia in the system the value of T_c determined on heating the sample from A to B depends upon the heating rate. The measured transition temperature is only equal to the thermodynamic equilibrium temperature of the transition at zero heating rate. To determine the equilibrium transition temperature a number of determinations of the transition temperature must be made at different heating rates and the transition temperature extrapolated to zero heating rate.

5 Constructing a kinetic model

A large number of solid state phase transformations can be described by a process known as nucleation and growth in which nuclei of a new phase are first formed at a particular rate followed by growth of the new phase at a faster rate. The formation of the new phase is thought to be caused by fluctuations, due to thermal agitations, which brings atoms in the parent phase to new positions corresponding to the product

phase. Formation of these embryos of the product phase results in an increase of the free energy of the system when their size is smaller than a certain critical size so they are usually converted back to the parent phase. Embryos that exceed the critical size are capable of continued existence and are called nuclei of the product phase. This process of nuclei formation is known as nucleation. A nucleus can now increase in size until it occupies the whole of the parent phase. This process, known as growth, involves the transfer of the parent phase to the product phase across the interface between the growing nucleus and the parent phase.

If we consider a reaction where $A \rightarrow B$, where nucleation takes place for a time τ and out of a total time t , then the volume of product phase B is:

$$dV_B(t) = dN_B \nu_B \quad (5)$$

where ν_B is the volume of a nucleus of phase B and dN_B , the number of nuclei formed per unit volume during the time $d\tau$, is given by:

$$dN_B(t) = \dot{N} d\tau V_A \quad (6)$$

where V_A is the volume of phase A and \dot{N} is the nucleation rate. The volume of a nucleus is given by:

$$\nu_B = \delta [\dot{G}(t - \tau)]^m \quad (7)$$

where \dot{G} is the growth rate and delta is a shape parameter. Combining equations 2, 3 and 4 and integrating to give the volume of phase A at time t we get:

$$V_B = \delta \int_0^t \dot{G}^m \dot{N} V_A (t - \tau)^m d\tau \quad (8)$$

assuming that \dot{G} and \dot{N} are constant and that the system is dilute we can obtain an expression for the amount transformed α :

$$\alpha(t) = \frac{V_B}{V_A} = \delta \dot{G}^m \dot{N} t^{m+1} = kt^n \quad (9)$$

This equation, known as the power law, has an obvious limitation: it predicts that the fraction transformed, or the volume of product, will increase to infinity. This is due to the assumption that the system is dilute, that is the volume of A does not decrease appreciably during the reaction. V_B is known as the extended volume. The real transformed volume is related to the extended volume by the equation:

$$V_{ext} = 1 - \exp(-V_B) \quad (10)$$

which was obtained by Avrami [19, 20, 21]. Or in terms of fraction transformed:

$$\alpha = 1 - \exp(-\alpha_{ext}) \quad (11)$$

which gives:

$$\alpha = 1 - \exp(-kt^n) \quad (12)$$

which is known as the Avrami equation. Let us consider the case where spherical nuclei of phase B are formed in the bulk of phase A and continue to grow as spheres. The volume of a nucleus is given by:

$$\nu = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi [\dot{G}(t - \tau)]^3 \quad (13)$$

and the number of nuclei formed in time t is given in equation 3. Combining these together we get:

$$\alpha = 1 - \exp\left(-\frac{4}{3}\pi \dot{N} \dot{G}^3 \int_0^t (t - \tau)^3 d\tau\right) \quad (14)$$

which gives:

$$\alpha = 1 - \exp(kt^4) \quad (15)$$

So: n is related to the shape of the nuclei of B growing in A. Taking logs of both sides of the Avrami equation gives:

$$\ln(1 - \alpha) = kt^n \quad (16)$$

and taking logs again:

$$\ln \ln(1 - \alpha) = \ln(t) + n \ln(t) \quad (17)$$

If the value of the shape parameter n is known then equation 13 may be used to determine the rate of transformation, otherwise equation 14 can be used to determine both the rate and shape parameter.

This derivation of the Avrami equation is well known [4] but serves to illustrate the general principles underlying the development of a kinetic model: chemical and physical knowledge is used to develop equation 8 which is then solved, experimental data is then fitted to the resulting expression in order to determine model parameter values. The physical meaning of these model parameters depends upon the physical and chemical model that was used to develop equation 8 and any assumptions that were made in order to solve it.

Once a kinetic model consistent with the data has been obtained the rate for various runs can simply be obtained from the time for half completion of the transformation $t_{\frac{1}{2}}$. Since, for example:

$$\alpha = 0.5 = \exp(-kt_{\frac{1}{2}}^n) \quad (18)$$

which can be rearranged to give:

$$k = \frac{\ln(2)}{t_{\frac{1}{2}}^n} \quad (19)$$

6 Determining the activation energy

The Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right)$$

(where k is the rate constant at temperature T , R is the gas constant, E is the activation energy and A is known as the pre-exponential factor) is well known [5]. It was developed for reactions in gases and liquids but has been applied to solid state

reactions [6, 7]. The activation energy is the energy barrier that the transformation has to overcome in order to produce the product phase and the magnitude of the activation energy is useful in helping us to understand the mechanisms by which the transformation proceeds as well as giving us a measure of the ease of the transformation. The activation energy can be determined from the Arrhenius equation by measuring the slope from a plot of $\ln(k)$ versus $1/T$ since:

$$\ln(k) = \ln(A) - \frac{E}{RT} \quad (20)$$

7 A demonstration of the above procedure

Three phases of ammonium chloride have been found to exist at atmospheric pressure [8]: phase I above about 183°C , phase II between 183°C and -30°C and phase III below -30°C . Phases II and III have the CsCl structure with chlorine ions at the corners of a cube and an ammonium ion in the centre. There are two possible orientations of the ammonium ion with nitrogen-hydrogen bonds lying along three fold axes (body diagonals). Direct octopole-octopole interactions between neighbouring ammonium ions favours parallel ordering (ammonium ions in the same orientation) while an indirect octopole-dipole-octopole interaction via the chlorine ions favours anti-parallel ordering [9, 10]. The ammonium ions in phase III are completely parallel ordered while no long range order exists in phase II [11]. Phase I has the NaCl structure with ammonium ions that are even less ordered than in phase II.

The transformation between phase I and phase II is reversible and thermodynamically first order [12]. A dilatometric investigation of this transformation by Poyhonen [13] established a transition temperature of 183.1°C .

7.1 Experimental

Analytical grade ammonium chloride was obtained from BDH Ltd. and ground in liquid nitrogen to give a fine powder made up of small white evenly sized crystals.

Data were collected using the energy-dispersive powder diffraction (EDPD) facility

at the UK synchrotron radiation source [14, 15] (figure 1). The diffraction angle was optimised, so as to have as few overlapping peaks as possible, at about 9.9° (figure 2); most of the low energy peaks are seen to be fully resolved and the background is virtually identical in both spectra.

Two methods of data collection were used: the MCA method [17] and the SCA method [18]. In the MCA method a series of whole diffraction patterns are collected for a set length of time each, and with a set time interval between them, during the course of the transformation (figure 3). The areas of the peaks of the two phases are then measured, using profile fitting, normalised and combined to give an estimate of the degree of transformation from one phase to the other. In the SCA method a number of strong, totally unoverlapped peaks are windowed electronically and all X-rays detected in these windows are counted for set time intervals during the course of the transformation (figure 4). An estimate of the degree of transformation was then made by normalising and combining these spectra. The MCA method has the advantage that peak fitting allows the study of materials with complex spectra with no unoverlapped peaks while the SCA method has the advantages that data can be collected more rapidly, due to lower computational overheads, and that less data analysis is required. Data were collected using both MCA and SCA methods although, due to the simplicity of the diffraction patterns in this case, the majority of the data were collected using the SCA method. Three diffraction peaks were monitored using the SCA method: the (110) peak of phase II and the (200) and (220) peaks of phase I.

A Linkham Scientific PH600 furnace, controlled by a PR600 controller, was used to vary the temperature of the sample. The furnace consists of a silver heating block, which encloses a platinum resistance thermometer, inside a water cooled jacket. X-rays pass through a sapphire window in the centre of the heating block. Samples were contained inside brass rings with thin glass slides as windows. These sample holders were held onto the heating block using two sprung loaded clips. Samples were one to two millimetres thick and about one centimetre in diameter. Dry nitrogen gas was bled into the furnace in order to give an inert atmosphere around the sample.

Data were collected both isothermally and non-isothermally. For isothermal data collection the sample temperature was rapidly changed to a target temperature and then data were collected in equal time slices. For non-isothermal data collection the temperature was changed at a slower constant rate and data were collected in equal time and therefore equal temperature slices while the temperature was rising. The former data were used for a kinetic analysis of the transformation and the latter for determining the transition temperature. Readings from an incident flux monitor were used to normalise all spectra [14].

7.2 Determination of the transition temperature

A plot of transition temperature versus ramp rate (figure 5) did not give the expected straight line. It has been suggested that the strong departure from linearity of these curves could be due to a Martensitic memory effect [16]. Alternatively, this behaviour could be due to the processes governing the kinetics of the transformation varying in different regions about the transition temperature. Such effects were not observed in the isothermal data presented in the next section of this paper. Despite the non-linear nature of these curves an accurate measure of the transition temperature was obtained without the need to use the curve fitting procedure of the previous author [13]. Nevertheless a transition temperature of $184.5 \pm 0.5^\circ\text{C}$ was determined.

7.3 Kinetic analysis

The isothermal data was found to fit the Avrami equation well (figure 6). Each curve gave a shape parameter of about three. The shape parameter was then fixed at three and the rate of transformation k was determined from the time for fifty per cent transformation ($t_{\frac{1}{2}}$ using equation 19. Values for the rate determined at different temperatures were then used to produce Arrhenius plots (figure 7) for heating and cooling measurements using pelletised and un-pelletised samples. Activation energies were then determined from the gradients of these graphs. The values obtained on heating and cooling were found to be the same within experimental error and an average value of $213 \pm 15 \text{ kJ mol}^{-1}$ was found.

8 Conclusions

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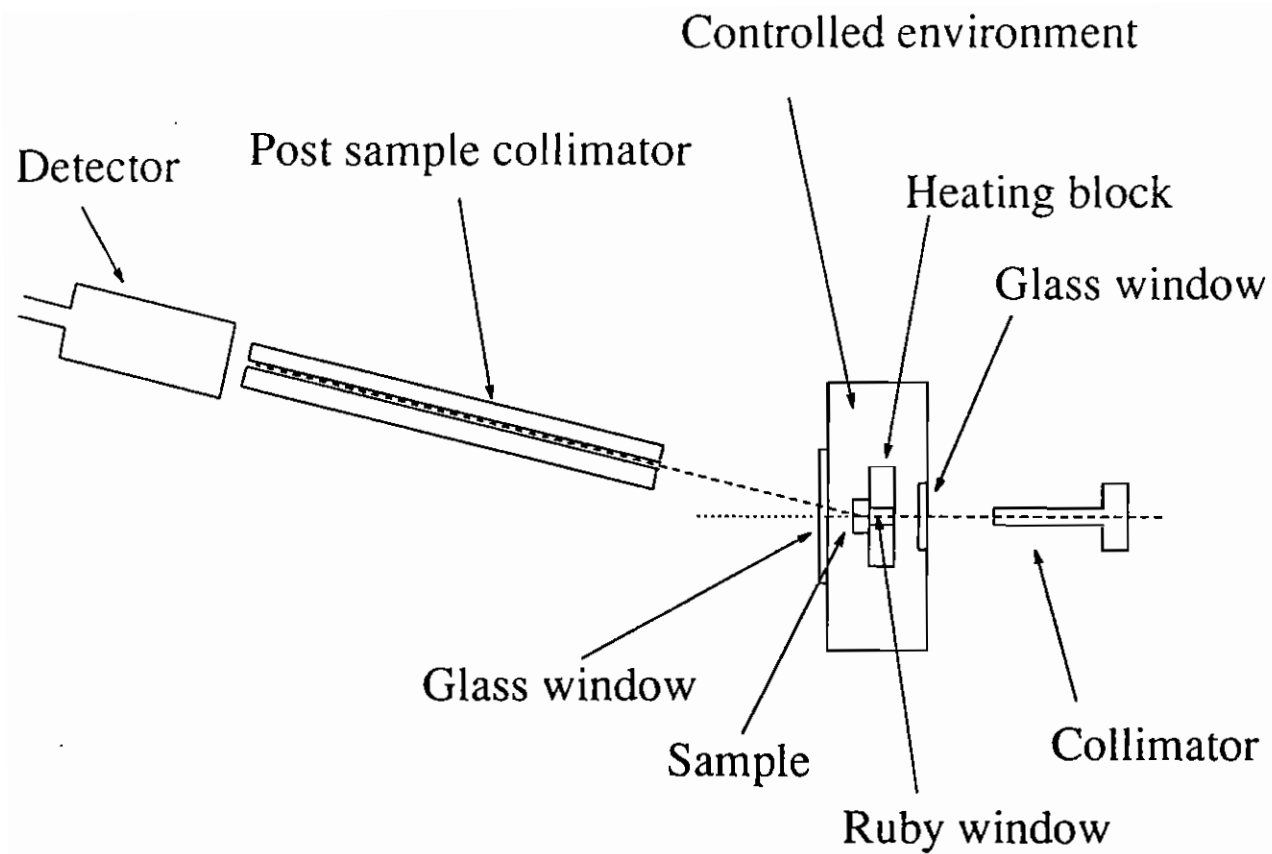


Fig.1

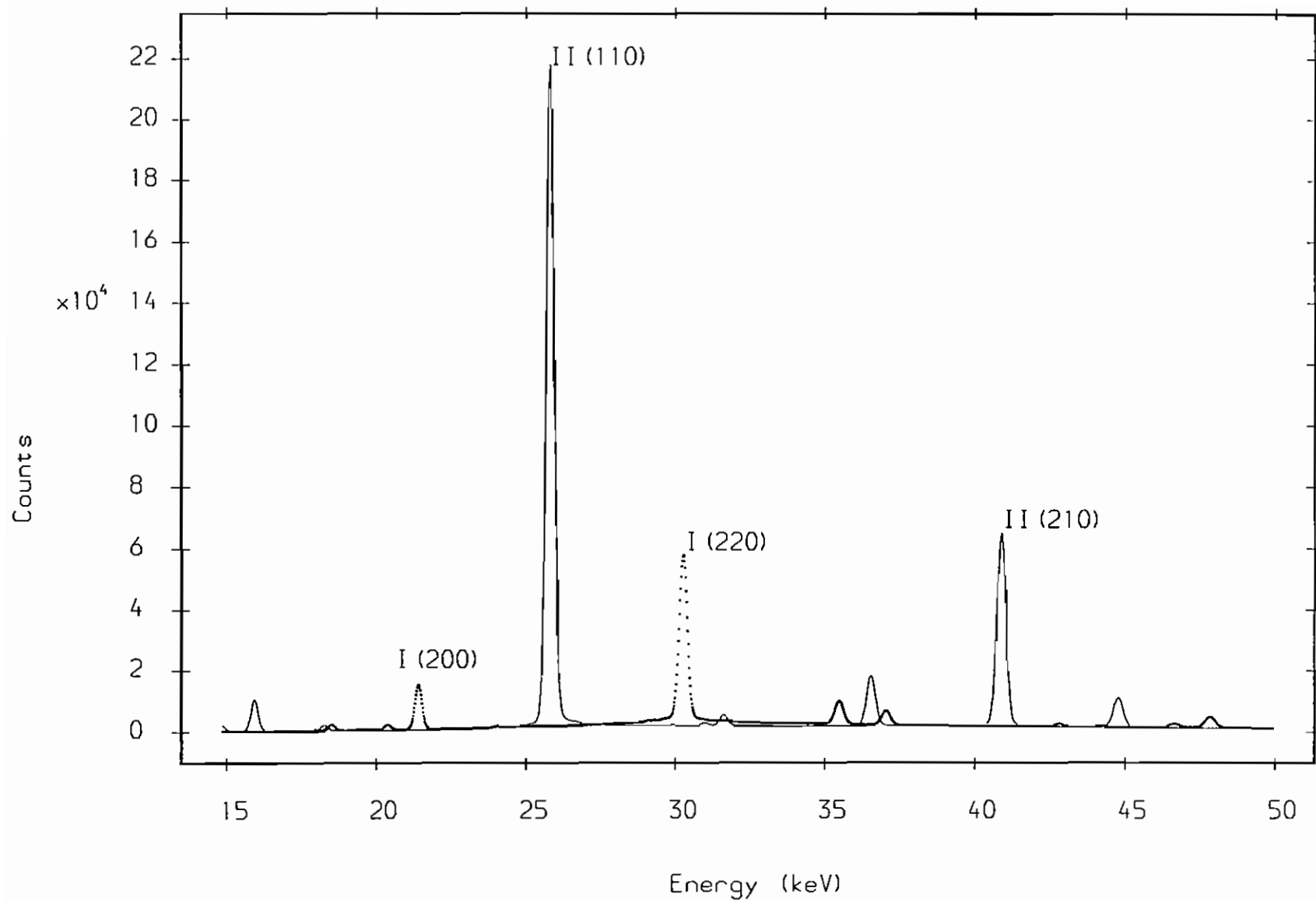


Fig.2

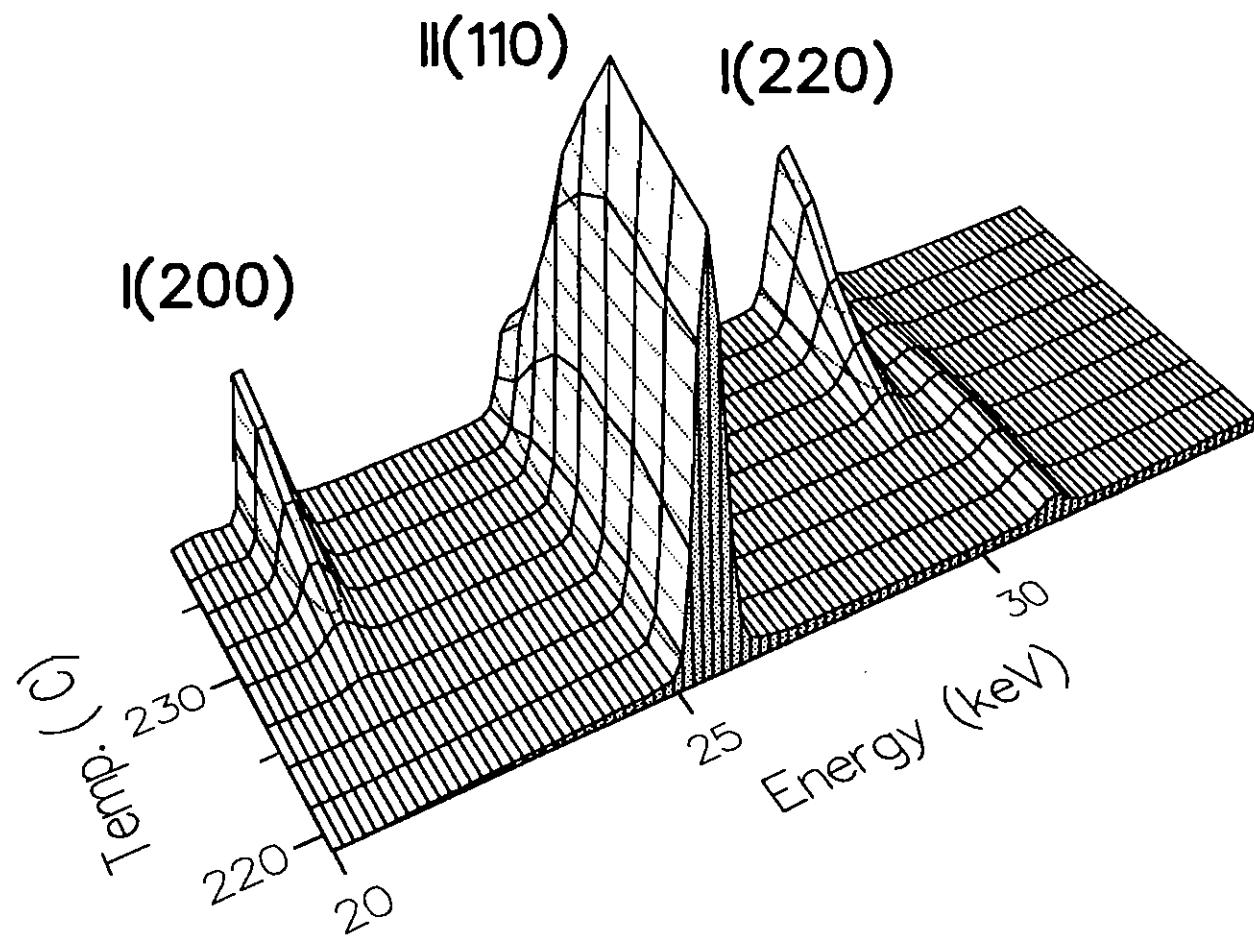


Fig.3

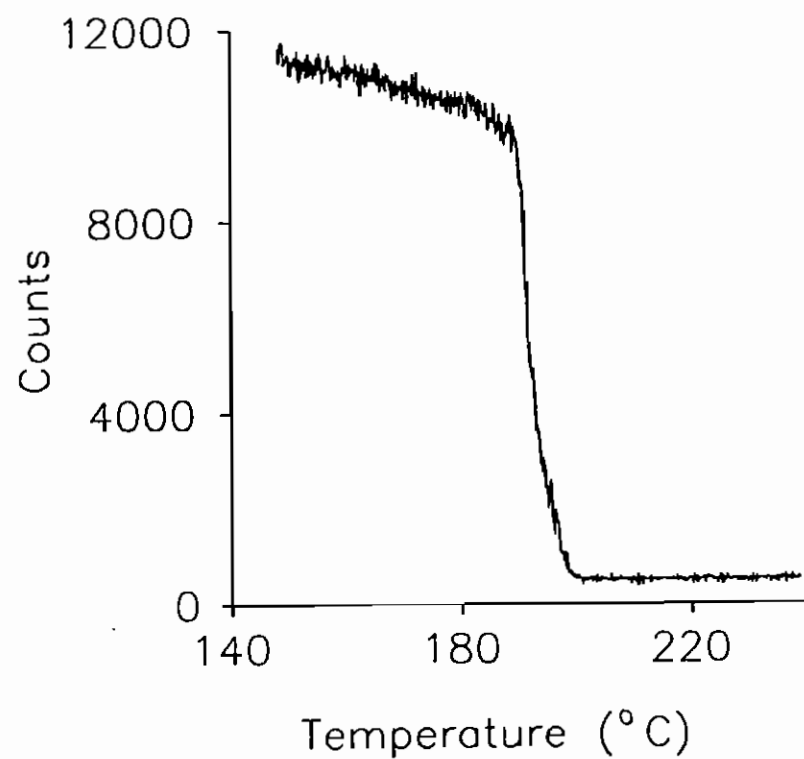


Fig.4

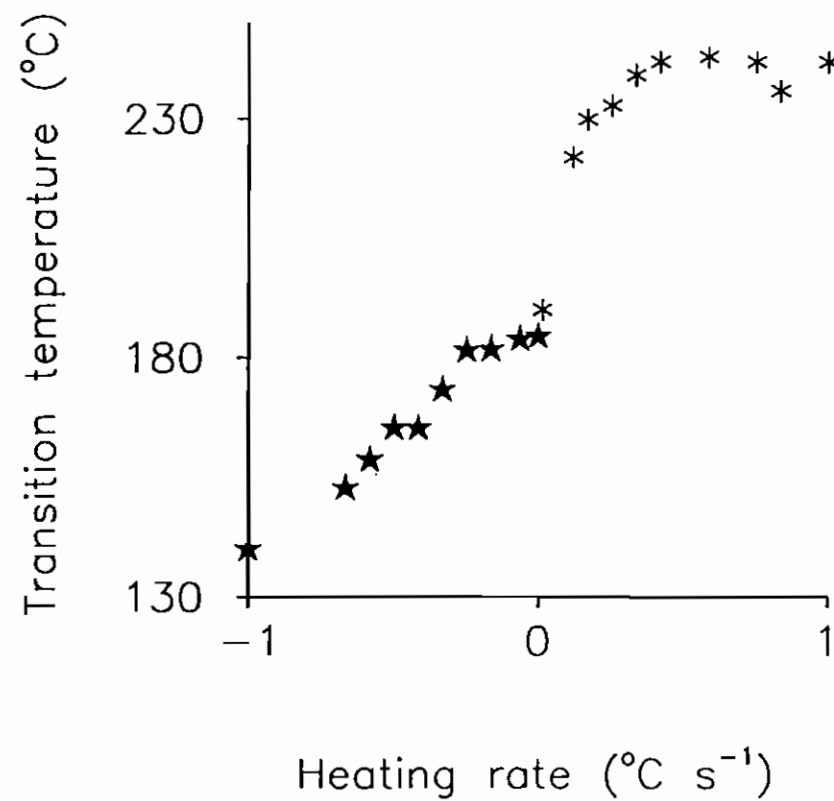


Fig.5