

## *Chapter 3*

# **A Review of the Influence of Magnetic Field on Phase Transformations**

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### **3.1 Introduction**

From an elaborate study of several reports appeared in the last few years, it is understood that magnetic field exerts perceptible influence on phase transformations in paramagnetic and diamagnetic materials. The use of fields for the design of materials with modified properties is gaining momentum at a speedy rate. However, the actual mechanism by which a magnetic field affects nucleation, crystal growth and other phase transitions is still puzzling.

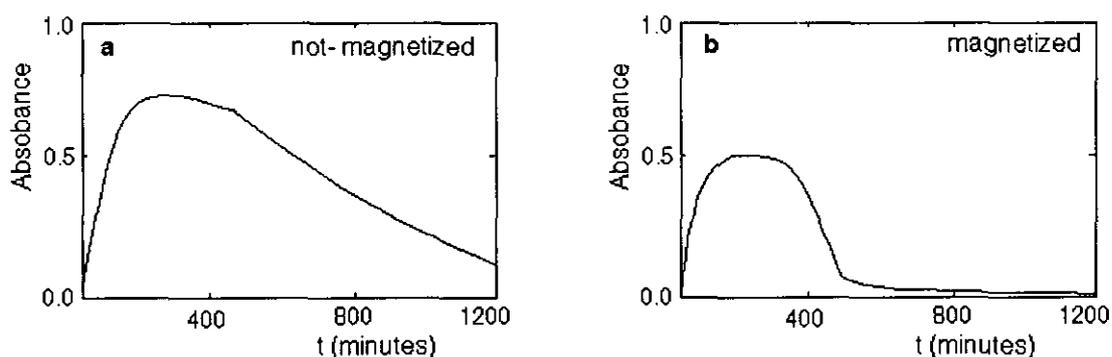
The earlier curiosity regarding the impact of magnetic field on matter other than ferromagnetic materials was connected with certain mysterious phenomena observed in animals and plants as a result of feeding them with magnetized water [1- 4]. The reported changes include increase in farm yields in both livestock and crop farming. It was found that even weak magnetic fields have the tendency to affect the flow through inorganic and organic membrane [5]. Other observations include the reduction of scale deposits on pipeline surface and the suppression of corrosion on metal surface. These studies are qualitative in nature and lack reproducibility and scientific rationale. This review castoffs any detailed discussion of reports that lack scientific footing. Also, for brevity of the discussion and for confining to the topic of crystallization process, the magnetic field influence on ferromagnetic materials in solid or solution phases will not be touched upon here. Therefore, the main theme of this chapter is the effect of magnetic field on the phase transformation of diamagnetic and paramagnetic materials. Particular attention will be on the nucleation and crystal growth in the presence of fields. A small sector will cover the field effects on the crystallization of proteins and other macromolecules. Before the chapter is wrapped up, a small review of the influence of field on the convective transport of materials in Czochralski and Bridgman techniques is presented.



### 3.2 Nucleation of Crystals in Solution

The early focal point in this topic was on the crystallization and precipitation of calcium carbonate. The experiments conducted by Pandalof et al. and [6] and Ellingson and Kristiansen [7] were qualitative. Dalas and Koutsoukos [8] reported a decrease of about 40 % in the formation of calcium carbonate with increasing strengths of the magnetic field. But the report lacks legitimacy, mainly because of the enormity of the field (18 T) they used, which is impossible with the conventional electromagnet described in the paper.

Higashitani et al. [9] conducted a systematic investigation to determine the effect of magnetic exposure on the nucleation of calcium carbonate crystals. Calcium carbonate crystals were formed by mixing dilute solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$ . The



**Fig. 3.1** Typical variation of absorbance for suspensions of nucleated  $\text{CaCO}_3$  particles;  $B = 0.45$  T, exposure time = 10 minutes (After Higashitani et al. [9]).

reactant solutions were exposed to magnetic fields up to 0.6 T before mixing. The magnetic field was generated by an electromagnet. The mixing of the solutions was carried out in the sample cell of a spectrophotometer. The variation of the absorbance due to the formation of  $\text{CaCO}_3$  particles in the cell was measured on a spectrophotometer at 350 nm wavelength of light. The temperature of the sample cell was held at  $30 \pm 0.1$  °C. Images of the sedimentary crystals were taken using an inverted microscope. The variations of absorbance  $A$  for unmagnetized and magnetized solutions are given in Fig. 3.1. From the systematic analysis of the absorbance curve, it was concluded that magnetic exposure of the reactants before they were mixed would suppress the formation of calcium carbonate crystals. It was also inferred that the

magnetic exposure would promote the growth of nucleated particles, provided that the field strength is greater than 0.3 T and the exposure time is greater than 10 minutes. Moreover, they observed that the change was due to the magnetic exposure of  $\text{Na}_2\text{CO}_3$  solution and not due to the exposure of  $\text{CaCl}_2$ . Furthermore, the study showed that the effect of magnetic exposure lasted up to 120 hours. The optical micrographs of the sedimented crystals in the experimental cell of the spectrophotometer showed that majority of the crystals were either parallelepipedic or spherical, both belonging to the calcite morphology. But in experiments with strong magnetic exposure, some needle like crystals of the aragonite morphology were also found. The XRD data of the crystals gave additional support to this notion of formation of aragonite morphology in strongly magnetized cases.

The changes brought about in the nucleation of a variety of crystals including calcium carbonate by the presence of magnetic field during the mixing of the reactants were studied systematically by Lundager Madsen [10, 11]. The strength of the field was fixed at 0.27 T. In all the experiments, one of the reactants was placed in the field generated in the gap between the pole pieces of the electromagnet before the second reactant was mixed with it. Crystals were examined using optical microscope. The fallouts of the experiments are consolidated in table 3.1. The calcium carbonate crystals formed with and without magnetic exposure were rhombohedral. However, magnetic exposure resulted in the formation of crystals with smaller size. For manganese carbonate, iron phosphate, cobalt phosphate, calcium sulfate and calcium oxalate the magnetic exposure did not make any change in the crystal formation. The magnesium phosphate crystals formed in field were smaller and were of more regular shape. In the case of calcium phosphate, apatite and brushite morphology were revealed in the absence of field. But, with field the brushite morphology was almost hidden. For zinc phosphate the nucleation rate and growth of crystals were slower. These data leads to the conclusion that the field effect is limited to the diamagnetic salts of weak acids and contradictory to the general belief, there was no effect on paramagnetic salts. Based on these observations a hypothetical argument was drawn, according to which, the magnetic field effect is due to the transfer of a proton from weak acids to water and subsequent orientation of the spin of the proton. But, since the field used is only 0.27 T



the orientation effect of proton spin would be negligible and it puts the hypothesis under suspicion.

**Table 3.1** Effect of magnetic field on the product crystals

Reactant 1	Reactant 2	Product	Effect of field
0.1 M CaCl <sub>2</sub>	0.1 M NaHCO <sub>3</sub>	CaCO <sub>3</sub> (calcite)	Smaller crystals
0.1 M MnSO <sub>4</sub>	0.1 M NaHCO <sub>3</sub>	MnCO <sub>3</sub>	None
0.1 M MgCl <sub>2</sub>	0.02 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 0.08 M (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	MgNH <sub>4</sub> PO <sub>4</sub> .6H <sub>2</sub> O	Smaller, more regular crystals
0.1M CaCl <sub>2</sub>	0.05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 0.05 M (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	CaHPO <sub>4</sub> .2H <sub>2</sub> O + Ca <sub>5</sub> OH(PO <sub>4</sub> ) <sub>3</sub>	Brushite almost absent (CaHPO <sub>4</sub> .2H <sub>2</sub> O)
0.1 M Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	0.05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 0.05 M (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .8H <sub>2</sub> O	None
0.1 M CoCl <sub>2</sub>	0.05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 0,05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .8H <sub>2</sub> O	None
0.1 M ZnSO <sub>4</sub>	0.05 M (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .4H <sub>2</sub> O(Hopeite)	Smaller, irregular crystals
0.1 M CaCl <sub>2</sub>	0.1 M (COOH) <sub>2</sub>	(COO) <sub>2</sub> Ca.H <sub>2</sub> O	None
0.2M CaCl <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	CaSO <sub>4</sub> .2H <sub>2</sub> O	None

In another experiment Lundager Madsen et al. [12] explored the magnetic influence on crystal formation of calcium phosphate out of calcium chloride and potassium dihydrogen phosphate. Their experiment was carried out at 20 °C under 0.27 T. It was found that magnetism has the power to accelerate the crystallization of calcium phosphates, in particular the basic forms octacalcium phosphate and hydroxyapatite, of which the latter is known for its slow growth rate under ordinary conditions. However, the dependence of the field strength on nucleation was not evident. Also they found that, at higher pH, the magnetic field had no influence on the crystallization mechanism.

The magnetic influence on the preparation of sodium hexafluorosilicate crystals was experimented by R. Chandrasekhar [13]. The crystals were prepared from sodium carbonate and hydrofluorosilicic acid and a magnetic field of strength 5.5 T was applied for 45 minutes immediately after the precipitation reaction. The microscopic nature of the crystals formed under different physicochemical conditions



were studied using SEM. The general nature of the magnetic exposure was an improvement in the crystal morphology and quality. Chandrasekhar explains the magnetic impact in the light of a hypothesis appeared in an early report [14], which regards the effect as the result of an increased strain generated by the field in the crystal lattice. This point will be elaborated later in the next section.

### **3.3 Growth Rate of Crystals in Solution**

Certain experiments present the growth rate of crystals in solution exposed to external magnetic fields. However, the observations are diverging in nature. For crystals like  $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  [15],  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  [16] and  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  [17], the application of field induced an increase in growth rate. The field did not bring forth any effect in the case of  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  [16] and ammonium sulfate salts of iron, zinc and copper [17]. ADP [18] and Rochelle salt [14,19] were the materials which exhibited decrease in growth rate. Mitrovic et al. [19] determined the change brought about by a magnetic field of strength 0.22 T in the growth rate of Rochelle salt crystals in the [010] direction. The crystal seeds were prepared in the absence of the field and their subsequent growth was carried out with the field applied perpendicular to the direction of solution flow. Three to ten crystals were considered in the experiment and the growth was monitored for 30 to 120 minutes. They found that the magnetic exposure would reduce the growth rate for majority of the crystals studied. Also, they observed that the growth rate of Rochelle salt crystals in the [010] direction is not dependent on the crystal orientation in the field. It was observed in this experiment that the growth rates of crystals in the absence and presence of field are better represented by a normal distribution at lower temperatures and higher supersaturations, whereas a gamma distribution is favored at higher temperatures and lower supersaturations. The changeover from one distribution to the other is attributed to the change in the growth mechanism and the changes on the surface of growing crystals. It was assumed that the changeover is due to the roughening of the Rochelle salt crystals. It allows one to say that the normal distribution is applicable at temperatures below the roughening temperature and the gamma distribution is applicable at higher temperatures. From a systematic analysis of the data obtained for the growth rate in the absence and presence of magnetic fields, it was found that the roughening of the surface occurred at a lower temperature due to



magnetic exposure. It is remarked in the report that the effect of magnetic field on the roughening temperature may be explained in terms of a change of crystal lattice parameters proposed in an earlier report [18]. This is in conformity with Bennema's [20] suggestion that a change in lattice parameters entails the change of the energy of a bond, which in turn alters the energy of the fluid-solid configuration in the interface and modifies the roughening temperature.

In another communication [21], Mitrovic has reported the magnetic influence on the growth rate of a paramagnetic salt  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . The application of magnetic field decreased the average linear growth rate in the direction normal to the (100) plane. Again, the roughening temperature was lower in samples grown under magnetic field. A conclusion was drawn from the two works, one on Rochelle salt and the other on manganese chloride, that the field effect on the growth rate was not due to the nature of magnetism (paramagnetic or diamagnetic) exhibited by the material. In another work reported by Mitrovic et al. [14] it was shown that an applied magnetic field might change the mosaic spread in Rochelle salt crystals and in turn influence the crystal growth rate. The mosaic spread reflects the total disorder including lattice plane mismatch, strain and defect content. In this experiment the growth rate of the crystals in the [010] direction, with and without magnetic field were measured. Mosaic spread was measured in crystals grown without a magnetic field and in portions of crystals that were grown for a certain time in an applied field. The mosaic spread  $\eta$  in the crystals were determined by the method of Andrews et al. [22], from the geometry of the Laue diffraction pattern, using the formula

$$l = \frac{2\eta d}{\cos 2\theta} \quad (3.1)$$

where  $l$  is the radial Laue spot extension,  $d$  is the distance from the flat film and sample and  $\theta$  is the reflection angle. The growth rate of the crystals was found to be inversely proportional to the mosaic spread. The qualitative explanation given by the authors for the observation follows:

"In the absence of the magnetic field, growth units of Rochelle salt-whether anions or cations, should have less entropic barriers to growth and would more easily assume energetically well defined sites in the lattice than in the presence of a magnetic field. The speed with which this occurs is governed by the overall driving force, along



with the availability of active steps or kinks in the growth face which function as preferential growth centers. At constant supersaturation the growth rate dispersion is dependent on the degree of strain developed during nucleation and on the growth process itself in each of the observed crystals. However, if a magnetic field were imposed, the ions of the Rochelle salt would be subjected to a considerable Lorentz force as they pass through the magnetic field. This may retard the incorporation of the growth units by disrupting the regularity of the lattice and modifying the energetics of the growth surface. At preferential growth sites or kinks in the lattice, the incoming growth units may adopt different bonding configurations, all of which are relatively close in energy. The lowest energy configuration would continue the growth of the most structured crystal. Alternative configurations will introduce imperfections, which may be magnified during further growth. The distortions introduced into the lattice are sufficient to create disordered growth surfaces, which produce sections of the crystal structurally different with respect to the lattice of the crystal grown without magnetic field. In this way strain becomes large and growth rate smaller.”

### **3.4 Effects on Crystallized Products**

K. Ohgaki et al. [23] studied the changes brought about by magnetic field on the XRD pattern and surface morphology of several inorganic crystals. The first step, in one of the methods he adopted, is the exposure of the saturated solution to a magnetic field of strength 2.4 T for 60 to 90 minutes. Then the solution is made supersaturated by gradually decreasing its temperature by 10 to 15 ° C. In the second method the reactants used to prepare a particular material were exposed to magnetic field of 1 T for one hour before they were mixed. The morphology and surface texture of the crystals formed were studied using scanning electron microscopy. X- ray diffraction patterns of the crystal lattice were recorded using powdered samples. This data is compared with the corresponding data from unmagnetized samples.

#### **3.4(i) Sodium nitrate crystals**

The surface texture at the microscopic level of the sodium nitrate crystals grown out of exposed solution was totally different from that grown without magnetization. In the unexposed sample the size of each grain was nearly 600 nm and they were not arranged in a particular fashion. However, the grains in the magnetized sample were one order less in size and they were arranged in a rectangular pattern. The



XRD pattern showed that the Bragg's angles of the largest peaks in the magnetized sample were 0.3 to 1 % smaller, indicating that the average diffraction distance of the crystals were greater due to magnetic exposure. The Laue patterns of the samples were suggestive of some strain imposed in the crystal. The NMR study of the samples indicated the presence of a small amount of water in the crystallized solute.

### 3.4(ii) Potassium sulfate and urea

In potassium sulfate crystals the shift in the Bragg's angles was not remarkable. However, the strongest and the second strongest peaks in the unmagnetized sample exchanged their positions mutually.

The most remarkable point in the case of urea was the change regarding the onset of crystallization. The crystallization in the unmagnetized solution occurred at 301 K while in the magnetized solution it started only at 291 K.

### 3.4(iii) Silver chloride

The most intense peak in the XRD pattern of the magnetically grown sample was Bragg shifted by about 0.42 degrees and the average diffraction distance was increased. The particles of the magnetized sample were almost uniform in size while in the unmagnetized case, particles of varying size were revealed.

### 3.4(iv) Barium sulfate crystals

In this case also, an increase in the average diffraction plane was exhibited by the sample grown under magnetic influence. However the change was strongly dependent on the aging time of the sample after the reaction (Fig. 3.2). The graph indicates that for small values of the aging time the Bragg's angle decreased and for

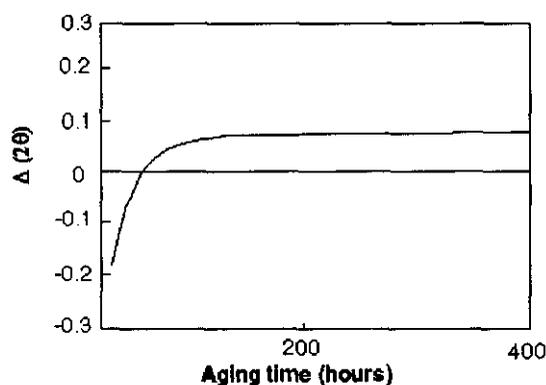


Fig. 3.2 Relation between Bragg's angle shift and aging time in barium sulfate crystals (After K Ohgaki et al [23]).

higher values of aging it was increased. The graph was drawn by studying the shifts of five peaks. It was found in most of the cases that the effect of exposure of the solutions remained for about five days.

### 3.5 Oriented Growth in Solution

Tokunaga et al. [24-26] employed the enormous fields generated by superconducting magnets to study the orientation effect of certain diamagnetic crystals belonging to organic and inorganic class. Benzophenone, trans-Azobenzene and potassium nitrate were the crystals studied. In all the cases, oriented growth was observed under strong fields.

In the experiment with trans-Azobenzene, ethanol was used as the solvent and a saturated solution of the material was allowed to stand in a small glass cell at 281 K. Crystals were obtained after 5 hours. They were of tabular rhombic form with the rhombic plane lying horizontal. The crystals were oriented in such a manner that their diagonal lines bisecting the acute angles of the rhombuses were perpendicular to the field (Fig. 3.3). The diamagnetic anisotropy of the crystals is cited as the agent, which brought about the oriented growth of the crystals in the applied magnetic field. For trans-Azobenzene, the molar susceptibilities along the crystallographic directions are:  $\chi_1 = -87.5 \times 10^{-6}$ ,  $\chi_2 = -130.2 \times 10^{-6}$  and  $\chi_3 = -83.1 \times 10^{-6}$ . It is claimed that the magnetization energy is minimum when the crystal is grown with its  $\chi_3$  axis parallel to the field direction. The experimental observation is in conformity with this.

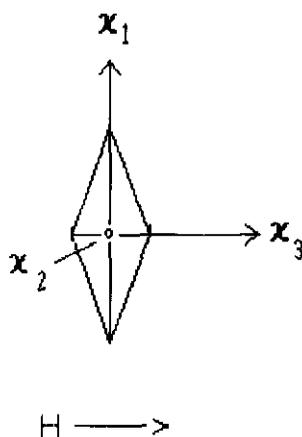


Fig. 3.3 Schematic diagram of the oriented trans- azobenzene crystal in the magnetic field (After M. Fujiwara et al. [26]).

For benzophenone crystals the space group is  $P2_12_12_1$  and the cell dimensions are  $a= 10.30$ ,  $b= 12.15$  and  $c= 8.00$  Å with four molecules in the unit cell. The molar magnetic susceptibilities are  $\chi_a= -88.0 \times 10^{-6}$ ,  $\chi_b= -88.6 \times 10^{-6}$  and  $\chi_c= -149.3 \times 10^{-6}$ . The crystals are in the form of columns elongated along the  $c$ -axis. In the magnetic field, the crystals were found growing with the  $c$ - axis perpendicular to the direction of field, which is shown as the configuration corresponding to the minimum of magnetic anisotropy energy.

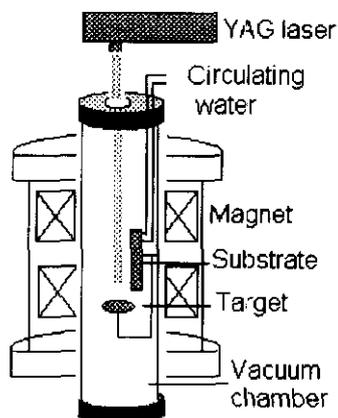
For potassium nitrate, the crystals formed were in the shape of columns lying horizontal. The typical crystal dimensions were  $30 \times 2 \times 2$  mm. The crystal system is orthorhombic. The cell dimensions are  $a= 6.4416$ ,  $b= 9.1573$ ,  $c= 5.44093$  Å. The molar magnetic susceptibilities are  $\chi_a= -35.6 \times 10^{-6}$ ,  $\chi_b = -29.7 \times 10^{-6}$  and  $\chi_c= -29.9 \times 10^{-6}$ . The X-ray studies proved that the crystals are oriented with the  $\chi_a$  axis perpendicular to the field direction. In potassium nitrate, the small magnetic anisotropy is explained to originate from the  $\text{NO}_3^-$  ion.

It is noteworthy that the magnetic anisotropy energy in benzophenone is one order greater than that in trans-Azobenzene and potassium nitrate. The fact that the enormous field did not make any change in the unit cell dimensions of the above three crystals is another remarkable point.

### 3.6 Oriented Growth in Thin Films

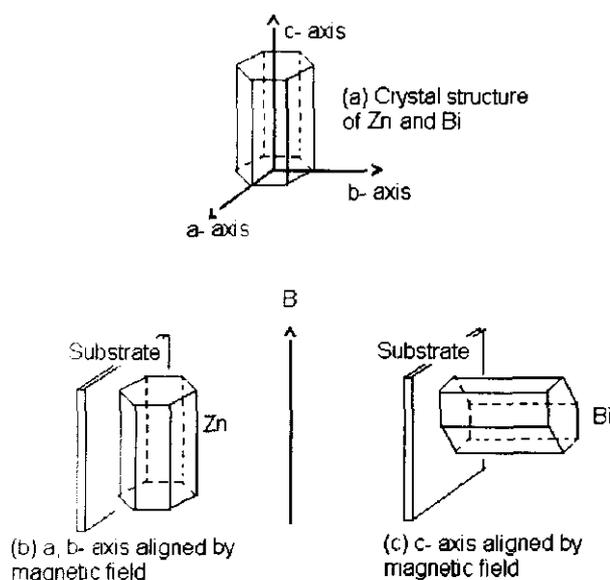
Tahashi et al. [27] investigated the effects of strong magnetic fields on the orientation in films deposited by the use of a YAG laser. The schematic view of the apparatus used is shown in Fig. 3.4. It consists of a vacuum chamber set in the 90 mm bore of a superconducting magnet. The target material vaporized by the use of YAG laser was deposited on a clean glass plate kept at  $10^{-3}$  Pa in the chamber. The orientation index of the deposited films was calculated from the intensity of X-ray diffraction lines measured by means of an X- diffraction analyzer. In the experiment reported, zinc and bismuth were used as the target materials.





**Fig. 3.4** Experimental view of the vacuum chamber for the coating of Zn and Bi in magnetic field (After Tahashi et al.[27]).

Both zinc and bismuth have hexagonal crystal structures and one expects magnetic anisotropy in the crystal depending on the direction. The theoretical part, formulated on the basis of a previous report predicted that, when a crystal is grown in a magnetic field, it would tend to align in a direction with the lowest magnetization energy. By the analysis of the magnetic susceptibilities of zinc and bismuth, the authors came to the conclusion that in the film grown under magnetic field the  $c$  axis of the crystal for zinc and the  $a$  or  $b$  axis for bismuth would be parallel to the direction of the applied field (Fig. 3.5), provided that the plane of the glass substrate is parallel to the field.



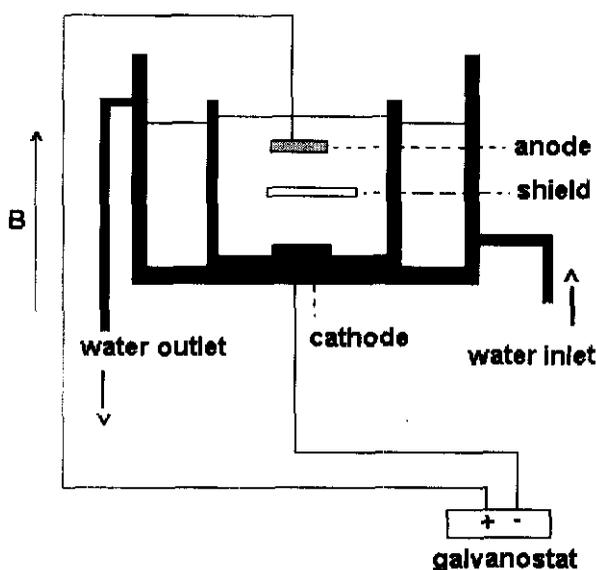
**Fig. 3.5** Favorable crystal orientation in zinc and bismuth under a magnetic field (After Tahashi et al. [27]).

The X-ray diffraction pattern of Zn deposited with and without field did not show any orientation whereas in the case of Bi the orientation effect was evident in the pattern of the XRD peaks. There were drastic changes in the grain size and surface texture of the Bi film grown under magnetic exposure. The film grown under magnetic field was constituted by larger particles than that grown without field. It was drawn from the experiment that the molar magnetic susceptibility value of about  $10^{-5}$  is not large enough to align Zn crystals in a magnetic field of 5 T. The magnetic field of 5 T is large enough to align the Bi crystals of molar magnetic susceptibility  $10^{-4}$ . It was also found that the crystal orientation due to magnetic field becomes tangible with an increase in the particle volume. Furthermore, the study indicates that the crystal orientation due to high magnetic field is related to the square of the magnetic field intensity. It was estimated that a magnetization energy difference over  $100 \text{ J/m}^3$  is required to reveal the crystal orientation.

Taniguchi et al. [28] have investigated the orientation effect of magnetic field in zinc electrodeposits. The schematic diagram of the experimental set-up is shown in Fig. 3.6. A clean copper plate was used as the substrate and a zinc plate was used as the anode. The magnetic field of strength 12 T was imposed on the cathode by means of a superconducting magnet. The electrodeposition was carried out under galvanostatic condition, with and without magnetic fields, which was applied perpendicular or parallel to the substrate. Crystal orientation indices of the electrodeposits were calculated from the data obtained by an X-ray diffraction analysis, compared with the JCPDS card.

When the magnetic field was applied perpendicular to the substrate, the orientation of the c- plane of the Zn crystals was revealed, which was in conformity with the theory formulated in the paper. The orientation indices of the c- plane increased with the strength of the applied field. On the other hand, when the field was applied parallel to the substrate, the orientation of the a- and b- planes were not observed, which was against the theoretical prediction. This discrepancy between the theory and the experiment was explained in terms of an overpotential generated by the flow in the solution by the Lorentz force.





**Fig. 3.6** Schematic diagram of the experimental set up for the electrodeposition of Zn (After Taniguchi et al. [28]).

### 3.7 Effect on Crystals Grown in Gel

The reports of the magnetic influence on crystals grown in gel medium are rather scarce. Sorensen and Lundager Madsen [12] studied the formation of calcium phosphate crystals in gel medium. The crystals were formed by the diffusion of calcium chloride into silica hydrogel containing phosphate ions. Fields of strength 0.08 to 0.3 T were applied. Positions of the Liesegang rings and single crystals formed in the gel column were studied and no significant change was observed in the magnetically exposed condition. However, it was observed that the nucleation of calcium phosphate crystals with brushite morphology was promoted in the presence of the field.

Another report of a gel growth experiment in the presence of magnetic field is due to Rahimkuty et al. [29]. In this work, the influence of magnetic field on the growth and thermal stability of strontium tartrate crystals was studied. Only weak fields (0.08 T) were employed. Here, a decrease in the speed of formation of crystals was observed and the authors attribute it to the decrease in the diffusivity of the ions due to the magnetic field. The most interesting point found as a result of the thermal studies of the samples is the revelation of the strong bonding of the water molecules locked up in the lattice of the crystal grown under magnetic field.

### 3.8 Crystallization of Proteins and Macromolecules

The early works on the influence of an external magnetic field were on certain poly- amino acids [30- 32], rhodopsin in retinal rod outer segment [33], DNA [34] and virus particles [35]. The major impact of the field was the orientation of the crystals with respect to the field direction. The orientation phenomenon was explained by means of the diamagnetic anisotropy of the macromolecular crystals [36, 37]. Sazaki et al. [38] studied the crystallization of lysozyme and horse-spleen ferritin under static and uniform magnetic fields of strength up to 10 T. Field caused changes in the number of crystals formed and the growth habit of the lysozyme crystals. Also majority of the tetragonal crystals were oriented with their c-axis parallel to the field. The tendency for orientation was more in solutions of higher concentrations. The 10 T field affected the habit of the crystal in such a way that the length of the crystals along the c- axis was less. For the ferritin crystals the number of nuclei were less in the solution kept under field. Thus it seems that the field affects different proteins in variant fashions as far as the nucleation rate is considered.

The orientation effect of lysozyme crystals was observed by another group of protein crystal growers with a field of 1.6T [39]. Hen-egg white lysozyme was dissolved in water and crystallization was carried out at 18 °C at a pH of 4.6 in the presence of 4 % (w/w) lysozyme and 3% NaCl. The crystallization vessel was placed between the pole pieces of an electromagnet. The orientation effect was explained in terms of the magnetic anisotropy of the diamagnetic lysozyme crystals. The experiment revealed that the crystals were nucleated in the bulk of the solution and they were sedimented to the bottom of the experimental cell after attaining sufficient weight. From the analysis of the sedimented crystals, it was possible to determine the time at which the crystals sedimented to the bottom.

In an extension of the work [40], Wakayama proposed an equation to determine the ratio of magnetically oriented crystals to the total number of crystals formed.

In another study [41] on the magnetic influence of lysozyme crystals, the magnetic force was superimposed on gravity in different ways. The magnetic force was resulted from the inhomogeneity of the field and the following conclusions were drawn:



- (i) when magnetic force was applied so as to oppose gravity the number of crystals formed decreased.
- (ii) when magnetic force was applied in the direction of gravity, the number of crystals formed increased.

In an elaborate study of the orientation effect of lysozyme in an external field of strength 1 T, Yanagya et al. [42] came to the conclusion that the orientation effect is negligible for small crystals, for, the magnetic anisotropy energy of small crystals is negligible. However, they proposed, depending on the geometry of the container, the crystals may grow sufficiently large to feel the anisotropy energy and can sediment to the bottom with appreciable orientation.

The orientation effect of protein crystals in external magnetic fields was explored by Sakurazawa et al. [43] using three different crystal forms of hen-egg white lysozyme, ribonuclease A and met-myoglobin crystals. Orientation of the crystals was observed in all cases with a magnetic field of 1 T. The growth rate of lysozyme crystals in external fields up to 11 T was studied by Yanagya et al. [44]. The effect of the field was to decrease the growth rate. Also the study showed that the dissolution of the crystals is less in the presence of the field.

The use of magnetic field for the improvement of protein crystal quality is reported by Lin et al. [45]. Snake muscle fructose-1, 6-bisphosphatase and human estrogenic 17  $\beta$ -hydroxysteroid dehydrogenase were the proteins used in the study. The crystalline quality was greater in crystals formed in the upper sector of the gap between the pole pieces of the magnet. In the upper portion, the magnetic field strength was 6 T and the gradient of the field in that region was sufficient to reduce the gravitational force on the sample by an amount 0.3 g.

### 3.9 Crystallization in Czochralski and Bridgman Techniques

The application of magnetic field in Czochralski and Bridgman techniques for yielding crystals with fewer imperfections has attained great attention in the last decade. For a review of the literature on this topic, the article written by Series and Hurlle [46] is recommended. Later, the effects of axial magnetic field on the growth striations of vertical gradient freeze gallium arsenide were studied by Park et al. [47]. They observed that the field could help the formation of perfect single crystals without any twin formation. The growth interface became straighter and flatter in the presence



of the external field of 0.12 T. A similar report on the influence of a field of strength 5 T on the solidification of HgZnTe crystals in a vertical solidification technique is due to Y.G. Sha et al. [48]. Effect of magnetic field on the periodic structure formation in Pb- Bi and Sn-Cd peritectic alloys is studied by H. Yasuda et al. [49]. It was found that a field of 10 T would change the band and spacing widths and the structure of the bands. Buoyant convection during Czochralski silicon growth due to the presence of a non-uniform axially symmetric magnetic field is seen in another report [50]. Improvement of crystal quality by the application of magnetic fields in the Bridgman crystal growth technique is also reported [51]. All the studies on this topic, mentioned above and reported elsewhere show that the use of a properly designed magnetic field during the growth of a solid phase in a melt phase would promote the crystalline quality of the final product.

### References

- [1] K. Syers, *Nz Farmer* 4 (1983) 24.
- [2] I.J. Lin, S. Nadiv, *Water Irrig. Rev.* 8 (1988) 16.
- [3] I.J. Lin, S. Nadiv, *ibid*, 9 (1989) 4.
- [4] I.J. Lin, J. Yotvat, *J. of Magn. Magn. Mater.* 83 (1990) 525.
- [5] I.J. Lin, S. Nadiv, *Magn. Sep. News* 2 (1988) 137.
- [6] L. Pandalof, R. Colale, G. Paiaro, *Chim. Ind.*, 69 (1987) 88.
- [7] F.T. Ellingson, H. Kristiansen, *Vatten* 35 (1979) 309.
- [8] E. Dalas, P.G. Koutsoukos, *J. Crystal Growth* 96 (1989) 802.
- [9] K. Higashitani, A. Kage, S. Katamura, K. Imai, S. Hatade, *J. Colloid and Interface Sci.* 156 (1993) 90.
- [10] H.E. Lundager Madsen, Report to DK Miljo A/S (1993).
- [11] H.E. Lundager Madsen, *J. Crystal Growth* 152 (1995) 94.
- [12] J.S. Sorensen, H.E. Lundager Madsen, *J. Crystal Growth* 216 (2000) 399.
- [13] R. Chandrasekhar, *J. Crystal Growth* 216 (2000) 407.
- [14] M.M. Mitrović, R.I. Ristić, I. Ćirić, *Appl. Phys. A* 51 (1990) 374.
- [15] F. Kuschel, A.N. König, *Cryst. Res. Technol.* 17 (1982) 801.
- [16] M. Scheiber, *J. Crystal Growth* 1 (1967) 131.
- [17] F. Kuschel, A.N. König, R. Gropp, *Cryst. Res. Technol.* 17 (1982) 793



- [18] B.B. Žižić, S.E. Božin, S.I. Žgarac, Ž.M. Nikolić, *J. Crystal Growth* 54 (1981) 439.
- [19] M.M. Mitrović, B.B. Žižić, M.L. Napijalo, *J. Crystal Growth* 87 (1988) 439.
- [20] P. Bennema, *J. Crystal Growth* 69 (1984) 182.
- [21] M.M. Mitrović, *J. Crystal Growth* 112 (1991) 171.
- [22] S.J. Andrews, J.E. Hails, M.M. Harding, D.W.J. Cruickshank, *Acta Crystallogr. A* 43 (1987) 70.
- [23] K. Ohgaki, Y. Makihara, H. Sangawa, *Chemical Engineering Science* 49 (1994) 911.
- [24] A. Katzuki, R. Tokunaga, S. Watanabe, Y. Tanimoto, *Chem. Lett* (1996) 607.
- [25] M. Fujiwara, R. Tokunaga, Y. Tanimoto, *J. Phys. Chem. B* 102 (1998) 5996.
- [26] M. Fujiwara, T. Chidiwa, R. Tokunaga, Y. Tanimoto, *J. Phys. Chem. B* 102 (1998) 3417.
- [27] M. Tahashi, K. Sassa, I. Hirabayashi, S. Asai, *Materials Transactions, JIM* 41 (2000) 985.
- [28] T. Tanuguchi, K. Sassa, T. Yamada, S. Asai, *Materials Transactions, JIM* 41 (2000) 981.
- [29] M.H. Rahimkutty, K. Rajendrababu, K.S. Pillai, M.R. Sudarsanakumar, C.M.K. Nair, *Bull. Mater. Sci.* 24 (2001) 249.
- [30] Y. Go, S. Ejiri, E. Fukada, *Biochim. Biophys. Acta* 175 (1969) 454.
- [31] E.T. Samulski, H.G.C. Berendsen, *J. Chem. Phys.* 56 (1972).
- [32] E.G. Finer, A. Darke, *J. Chem. Soc., Faraday Trans. 1* 71 (1975) 984.
- [33] M. Chabre, *Proc. Natl. Acad. Sci. USA* 75 (1978) 5471.
- [34] M. Suzuki, H. Nakamura, *Proc. Jpn. Acad. Phys. Biol. Sci.* 71 (1995) 36.
- [35] M. Hirai, T. Takizawa, S. Yabuki, *Phys. Rev. E* 51 (1995) 1236.
- [36] D.L. Worcester, *Proc. Natl. Acad. Sci. USA* 75 (1978).
- [37] L. Pauling, *Proc. Natl. Acad. Sci. USA* 76 (1979) 2293.
- [38] G. Sazaki, E. Yoshida, H. Komatsu, T. Nakada, S. Miyashita, K. Watanabe, *J. Crystal Growth* 173 (1997) 231.
- [39] M. Ataka, N.I. Wakayama, *J. Crystal Growth* 173 (1997) 592.
- [40] N.I. Wakayama, *J. Crystal Growth* 191 (1998) 199.
- [41] N.I. Wakayama, M. Ataka, H. Abe, *J. Crystal Growth* 178 (1997) 653.



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- [42] S. Yanagya, G. Sazaki, S.D. Durbin, S. Miyashita, T. Nakada, H. Komatsu, K. Watanabe, M. Motokawa, *J. Crystal Growth* 196 (1999) 319.
- [43] S. Sakurazawa, T. Kabota, M. Ataka, *J. Crystal Growth* 196 (1999) 325.
- [44] S. Yanagya, G. Sazaki, S.D. Durbin, S. Miyashita, T. Nakada, H. Komatsu, K. Watanabe, M. Motokawa, *J. Crystal Growth* 208 (2000) 645.
- [45] S.X. Lin, M. Zhou, A. Azzi, G.J. Xu, N.I. Wakayama, M. Ataka, *Biochem. Biophys. Res. Com.* 275 (2000) 274.
- [46] R.W. Series, D.T.J. Hurle, *J. Crystal Growth* 113 (1991) 305
- [47] Y.J. Park, E.K. Kim, M.H. Son, S.K. Min, *J. Crystal Growth* 156 (1995) 487.
- [48] Y.G. Sha, C.H. Su, S.L. Lehoczky, *J. Crystal Growth* 173 (1997) 88.
- [49] H. Yasuda, K. Tokieda, I. Ohnaka, *Materials Transactions, JIM* 41 (2000) 1005.
- [50] Y.Y. Khine, J.S. Walker, *J. Crystal Growth* 147 (1995) 313.
- [51] J.S. Walker, *J. Crystal Growth* 192 (1998) 318.

