

## 1. General Introduction

Translational lattice periodicity is one of the basic characteristics of the concept of crystal [1, 2]. It is known, however, that some kinds of crystals cannot be described by a single translational period but require two or more sublattices which have incommensurate lattice lengths with each other (Fig. 1. 1 (b)). This structure is so-called incommensurate (IC). In dielectric compounds, especially ferroelectrics, the incommensurate structure was discovered in  $\text{NaNO}_2$  [3] in early 1960s and then in  $\text{SC}(\text{NH}_2)_2$  [4]. Recently, the IC phase was found at low temperatures in many of  $\text{A}_2\text{BX}_4$ -type compounds, e.g.,  $\text{K}_2\text{SeO}_4$  [5] and  $\text{Rb}_2\text{ZnCl}_4$  [6], with the  $\beta$ - $\text{K}_2\text{SO}_4$ -type structure, whose static and dynamic properties have been investigated by various methods [1]. Then, the name “incommensurate structure” has frequently been used since the discovery of the structure of the charge density wave (CDW) in low-dimensional conductors in the 1970s [7]. IC crystals are roughly divided into two main categories which are A) modulated crystals and B) composite crystals. The modulated crystals have the modulation of density, displacement, orientation and so on to the underlying period [1] while they have homogeneous chemical composition. These modulated incommensurate materials are further classified into several sub-categories according to the types of modulation [1]: 1) Low-dimensional conductors with the CDW. 2) Magnets with the orientational modulation of spins. 3) Dielectric materials with the structural modulation due to the displacement or the orientation of atoms, ions or moleculars. 4) Materials with periodic or quasiperiodic defects on the interface such as stacking faults, antiphase boundaries and shear planes. 5) Liquid crystals with the orientational

modulation of molecules in the smectic- $C_A^*$  phase. On the other hand, the composite crystals have the intergrowth structure and crystallize in the stacking of two or more substance with different periodicities in an unit cell level []. These materials are also classified more detail into a few sub-categories by types of intergrowth [1]: 1) Linear intergrowth compounds which are usually called the composite crystals. 2) Intercalation compounds. 3) Molecular monolayers adsorbed on a clean surface of crystals such as graphite. The example of compounds which belong to the above material groups with the incommensurate structure are listed in Table 1. 1.

**Table 1. 1** Classification of material groups with the incommensurate structure.

Group	Materials
A-1) Low-dimensional conductors (CDW)	TTF-TCNQ [8], $(\text{TaSe}_4)_2\text{I}$ [9]
A-2) Magnets (magnetic spiral modulation)	Cr [10], $\text{EuAs}_3$ [11] and CuMn alloy [12]
A-3) Dielectric materials	$\text{NaNO}_2$ [3], $\text{SC}(\text{NH}_2)_2$ [4], $\text{K}_2\text{SeO}_4$ [5] and $\text{Sr}_2\text{Nb}_2\text{O}_7$ [13]
A-4) Interface	$\text{Ti}_{1+x}\text{Al}_{3-x}$ alloy [14]
A-5) Liquid crystals (smectic- $C_A^*$ phase)	MHPOBC [15]
B-1) Composite crystals	$\text{Hg}_{3-\delta}\text{AsF}_6$ [16] and $(\text{PbS})\text{VS}_2$ [17]
B-2) Intercalation compounds	graphite-(Cs, Rb and K) [18]
B-3) Adsorbed monolayer	graphite-Kr [19]

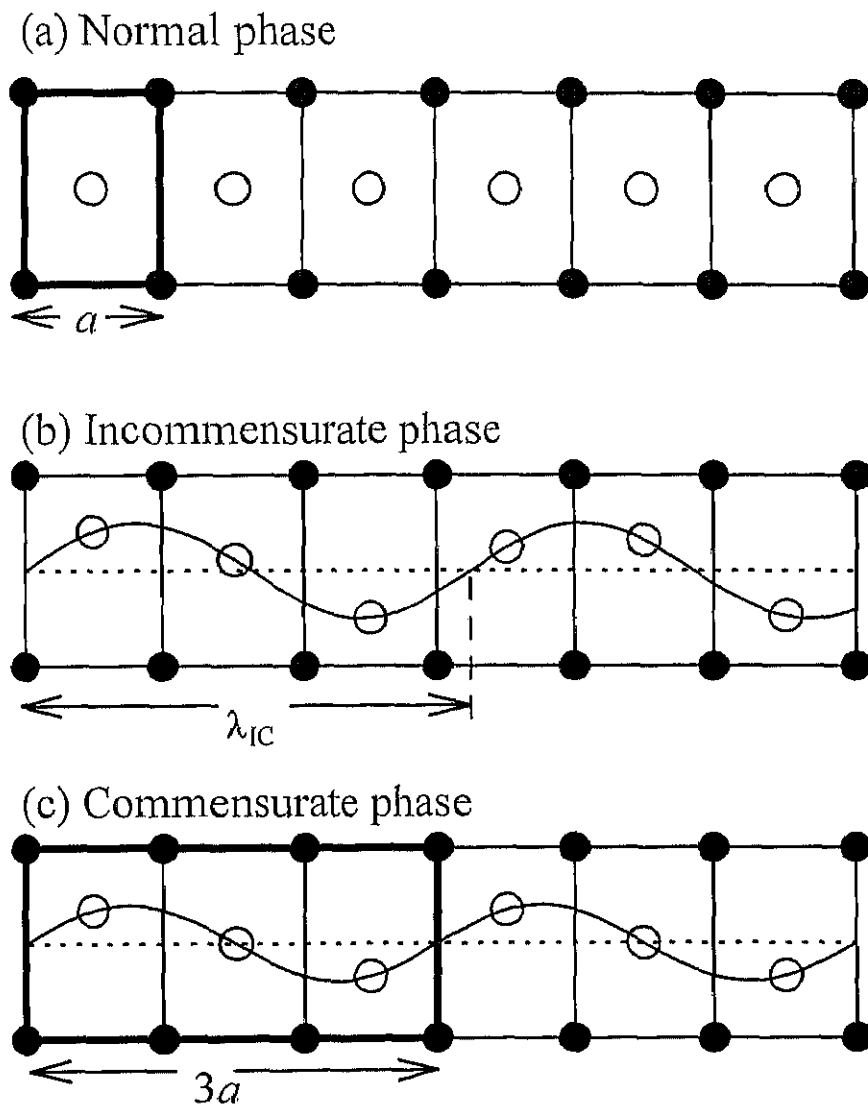


Fig. 1. 1 Atomic arrangements in (a) normal, (b) incommensurate and (c) commensurate phases obtained in the cooling process. Here,  $a$  is a unit lattice length,  $\lambda_{IC}$  is the wavelength of the incommensurate modulation. Bold lines represent unit lattices in the normal and the commensurate phases. The structure in the IC phase can not be described by a single translational period of the unit cell, because the wavelength  $\lambda$  of the modulation is not a rational multiple of the unit lattice length  $a$ .

The IC structure in the dielectric materials (group A-3) appears in a particular temperature range between the normal (N) phase which is a high-temperature phase with no modulation, and the commensurate (C) phase which is a low-temperature phase with the commensurate modulation as shown in Fig 1.1 (a) and (c), respectively. Usually, the N-IC phase transition is the second order and the IC-C transition is the first order.

In this work, the  $\text{Cs}_2\text{MX}_4$  family is taken up and  $^{133}\text{Cs}$  NMR is measured to understand the mechanisms which cause the IC modulation. This family has an advantage that systematic comparison with each other is possible because a lot of compounds belonging to this family have been reported. Some of them take the  $\beta\text{-K}_2\text{SO}_4$  structure in the high-temperature phase. Some compounds with the  $\beta\text{-K}_2\text{SO}_4$  structure form the IC phase at low temperatures.

$^{133}\text{Cs}$  NMR is a convenient method to study mechanisms of phase transition because this method affords quite sensitive probes to the electronic structure around the nucleus such as nuclear quadrupole interactions. Furthermore,  $^{133}\text{Cs}$  NMR has a high sensitivity because of its high natural abundance (100 %) and short spin-lattice relaxation time ( $T_1$ ).

At first, the dynamic behavior of crystal lattice in a group ( $\text{Cs}_2\text{CdBr}_4$ ,  $\text{Cs}_2\text{HgBr}_4$ ,  $\text{Cs}_2\text{CdI}_4$  and  $\text{Cs}_2\text{HgCl}_4$ ) having analogous IC phases will be discussed in chapter 2. Especially the critical fluctuation in the lattice near the N-IC phase transition and characteristic dynamics in the IC phase are compared with each other in measured substances. The similarity and difference are discussed in detail concerning with properties of chemical bond formed between halogen and Cs atoms.

In chapter 3, the thermal expansion in crystals and  $^{133}\text{Cs}$  NMR spectra and relaxations are compared between the group with the  $\beta\text{-K}_2\text{SO}_4$  structure without the

analogous IC phase ( $\text{Cs}_2\text{ZnCl}_4$ ,  $\text{Cs}_2\text{ZnBr}_4$  and  $\text{Cs}_2\text{ZnI}_4$ ) and the group with the  $\text{Sr}_2\text{GeS}_4$  structure ( $\text{Cs}_2\text{CdI}_4$  and  $\text{Cs}_2\text{HgI}_4$ ). These results are discussed in connection with the covalency between halogen and Cs atoms.

In chapter 4, the comparison between the  $\text{Cs}_2\text{MX}_4$  group with ( $\text{Cs}_2\text{CdBr}_4$ ,  $\text{Cs}_2\text{HgBr}_4$ ,  $\text{Cs}_2\text{CdI}_4$  and  $\text{Cs}_2\text{HgCl}_4$ ) and those without the analogous IC phase ( $\text{Cs}_2\text{ZnCl}_4$ ,  $\text{Cs}_2\text{ZnBr}_4$  and  $\text{Cs}_2\text{ZnI}_4$ ) is attempted. In conclusion, microscopic mechanisms of the appearance of the IC phase are discussed.

## References in Chapter 1

- [1] H. Z. Cummins, *Phys. Rep.*, **185** (1990) 211 and references therein.
- [2] R. Blinc, *Phys. Rep.*, **79** (1981) 331.
- [3] S. Tanisaki, *J. Phys. Soc. Jpn.*, **16** (1961) 579.
- [4] Y. Shiozaki, *Ferroelectrics*, **2** (1971) 245.
- [5] M. Iizumi, J. Axe, G. Shirane and K. Shimaoka, *Phys. Rev.*, **15** (1977) 4932.
- [6] S. Sawada, Y. Shiroishi, A. Yamamoto, M. Takashige and M. Matsuo, *J. Phys. Soc. Jpn.*, **43** (1977) 2099.
- [7] J. A. Wilson, F. J. Disalvo and S. Mahajan, *Adv. Phys.*, **24** (1975) 117.
- [8] P. Bak and V. J. Emery, *Phys. Rev. Lett.*, **36** (1976) 978.
- [9] T. Sekine, T. Seino, M. Iizumi and E. Matsuura, *Solid State Commun.*, **53** (1985) 767.
- [10] H. Meekes, *Phys. Rev. B* **38** (1988) 5924.
- [11] T. Chattopadhyay, P. J. Brown, P. Thalmeier and H. G. v. Schnering, *Phys. Rev. Lett.*, **57** (1986) 372.
- [12] S. A. Werner, J. J. Rhyne and J. A. Gotaas, *Solid State Commun.*, **56** (1985) 457.
- [13] K. Ohi, M. Kimura, H. Ishida and H. Kakinuma, *J. Phys. Soc. Jpn.*, **46** (1979) 1387.
- [14] A. Loiseau, G. van Tendeloo, R. Portier and F. Ducastelle, *J. Phys. (Paris)*, **46** (1985) 595.
- [15] I. Muševic, R. Blinc, B. Žekš and M. Čopič, *Phys. Rev. Lett.*, **71** (1993) 1180.
- [16] J. D. Axe and P. Bak, *Phys. Rev. B* **26** (1982) 4963.
- [17] G. A. Wieggers, *Prog. Solid State Chem.*, **24** (1996) 1.
- [18] R. Clarke, J. N. Gray, H. Homma and M. J. Winokur, *Phys. Rev. Lett.*, **47** (1981) 1407.
- [19] A. Q. D. Faisel, M. Hamichi, G. Raynerd and J. A. Venables, *Phys. Rev. B* **34** (1986) 7440.