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PHASE TRANSITIONS IN INCOMMENSURATE
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Masashi IIZUMI

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PHASE TRANSITIONS IN INCOMMENSURATE INSULATORS

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This review is an attempt to summarize the experimental results essential for understanding the incommensurate phases in the insulating crystals, especially those of the K_2SeO_4 type. In order to understand the wide variety of the incommensurate characters exhibited by this type of crystals a lattice dynamical origin is discussed.

Keywords: Phase Transition, Incommensurate Phase, K_2SeO_4 ,
Lattice Dynamics, Insulators, Ferroelectric Crystals,
Ferroelastic Crystals.

Review paper presented at the XIIth Congress of International Union of Crystallography held in Ottawa, Canada from 16 to 25, August, 1981.

不整合不導体の相転移

日本原子力研究所東海研究所物理部

飯泉 仁

(1981年11月20日受理)

不導体結晶，特にセレン酸カリ型結晶における不整合相を理解するのに重要な実験結果をまとめて議論した。またこの種の結晶の示す不整合構造の多様さを説明するため，格子力学的な起源について議論した。

この総合報告は第12回国際結晶学会議（カナダ，オタワ市，1981年8月16～25日）において発表されたものである。

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1. INTRODUCTION

Since we carried out neutron scattering measurements on potassium selenate (K_2SeO_4) and found an incommensurate (INC) phase in this crystal¹⁾, a lot of insulating crystals have been found to have INC phases in certain ranges of temperature and their properties have been studied by various methods. Prior to K_2SeO_4 , sodium nitrite and thiourea had been only two known examples of the INC insulators and they had been regarded as quite an exceptional phenomenon. Since then, however, we have seen such a rapidly growing number of the INC insulators that we have become aware that they are not uncommon among insulating crystals.

This recognition comes not only from the mere increase of the number of examples but also from a theoretical basis. The so-called Lifshitz condition is now recognized to have such a positive meaning to the INC structures that in a certain type of phase transition an INC structure is required by this condition from the symmetry reasoning²⁾. We will not go into the details of this problem here. Let me just point out that one can use the condition as a guiding principle to find INC structures and one can even predict the existence of an INC phase in the vicinity of a phase transition below which the crystal structure has been known to be commensurate (COM). The INC phase transition in $RbD_3(SeO_3)_2$ is a typical example found in this way³⁾. Also this guiding principle happened to lead us to the discovery of an INC lattice modulation existing in the ferroelectric phase of ammonium Rochelle salt⁴⁾.

Among the various types of the INC insulators we are especially interested in the specific type of crystals which manifests the ferroelectric or ferroelastic properties closely associated with the INC properties. They are called INC ferroelectrics (or ferroelastics). This terminology is somewhat misleading because the ferroelectric phases below the Curie temperatures are not usually incommensurate but are merely related to the INC phases in another temperature ranges.

Among the various INC ferroelectrics and ferroelastics known until now K_2SeO_4 and related crystals constitute the majority group. This family of crystals has common formula, A_2BX_4 , and common high-temperature crystal structure. In the formula A stands for the alkaline metal ions, ammonium group or tetramethyl-ammonium group ($N(CH_3)_4$ which is hereafter to be abbreviated as TMA). The group BX_4 is SeO_4 , BeF_4 or MX_4 in which M stands for Zn, Cu, Fe etc. and X for Cl or Br.

In the present paper I would like to consider only this family of crystals which not only demonstrates the most typical behavior of the INC ferroelectrics but also reveals an interesting wide variety of the INC properties. The brief review of the INC phase transitions in this type of crystals in Sec. 2 may bring out the following questions:

- 1) Why is this type of crystals rich in the INC structures?
- 2) Why do the similar crystals show such behavior rich in variety?

Although I do not have any successful answer to those questions, I would like to consider them in Sec. 3 from a lattice-dynamical point of view which, I hope, supplies some

clue to answer the questions.

2. INCOMMENSURATE PHASE TRANSITIONS IN THE K_2SeO_4 FAMILY

The crystals belonging to the K_2SeO_4 type are roughly divided into a few groups as shown in Fig.1. Potassium selenate was first studied¹⁾ and is still the best investigated system. It shows the simplest behavior of the family. Therefore we take it as a prototype. Rubidium tetrachlorozincate (Rb_2ZnCl_4) and others exhibit very similar behavior to K_2SeO_4 . Ammonium fluoroberyllate (AFB) belongs to a different group. TMA tetra halides of various metal elements are now being actively studied. They have revealed various interesting aspects of the compounds belonging to this family. The Cu and Mn salt is related to K_2SeO_4 and AFB, respectively, and the rest falls in another group. The names in the parentheses show typical authors whose work I am going to review in this paper.

2.1 K_2SeO_4 — Prototype

Let's begin with the prototype - K_2SeO_4 . At room temperature it takes the so called β - K_2SO_4 structure and this is isomorphous with the well known ferroelectric substance: ammonium sulphate, $(NH_4)_2SO_4$. The figure 2 shows schematically the crystal structure of K_2SeO_4 at room temperature. The unit cell contains four formula units. If we take SeO_4 tetrahedron as a rigid unit all the constituents lie either at the

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level $z = 1/4$ and $3/4$. The crystallographic axes shown here are different from those adopted recently by a common consent in Japan. We must exchange a and c according to that convention, which is in accord with the pseudo-hexagonal symmetry of this structure. In the present paper I would like to follow this convention. However let me use some old figures, in which a is still the modulation direction.

The essential features of the phase transitions in K_2SeO_4 are summarized in Fig.3. There are two phase transitions in K_2SeO_4 . Firstly at $T_1 = 128$ K a second order phase transition takes place and an INC structure appears with the modulation wave vector in the c direction of the crystal. This gives rise to satellite reflections at INC positions in the reciprocal space. The positions are given by the modulation wave vector which is expressed as a deviation from a COM structure:

$$q_1 = q_c + \delta \quad .$$

Since an INC structure is always very close to a certain COM structure⁵⁾, it is convenient to consider the INC structure by the deviation from the COM one. The COM wave vector q_c is equal to $1/3$ in this case. The magnitude of δ decreases smoothly with decreasing temperature and at T_c the second phase transition takes place. This phase transition is of first order and δ becomes zero discontinuously. This phase transition is called the INC to COM phase transition or lock-in transition. The order parameter of the successive phase transitions is the amplitude of the modulation which is observed as a satellite intensity and it changes as it is shown

in Fig.3(c).

One of the important features of the INC insulators is that the secondary and higher lattice distortions are induced through the anharmonic effect and they play an essential role in introducing macroscopic quantities, such as spontaneous polarization or strain, in the COM phase. The secondary lattice distortion is already induced even in the INC phase and is modulated with a long periodicity. Then below T_C the modulation disappears and the secondary lattice distortion transforms into a macroscopic quantity; in the case shown in Fig.3 it is the spontaneous polarization. The nature of the induced quantities is different according to the order of anharmonic terms and the kind of coupled quantities as we will see in the following examples.

2.2 Rb_2ZnCl_4 and the like

Rubidium tetrachlorozincate (Rb_2ZnCl_4)⁶⁾, Rb_2ZnBr_4 ⁷⁾ and K_2ZnCl_4 ⁶⁾ are isomorphous with K_2SeO_4 and exhibit the same sequence of phase transitions. So I will not go into the details here. I just show the temperature changes of δ in Fig.4. In this figure the temperature scale is reduced in unit of T_i of each crystal. Since T_i of the compounds in the present group is far higher than that in K_2SeO_4 , the INC phase has a wide temperature range which is suitable for studying the details of the INC structure. Rb_2ZnBr_4 exhibits a very peculiar behavior: δ is essentially temperature-independent for more than 140 degree and then it changes very rapidly being

accompanied by a great hysteresis. This part was later examined carefully and it was pointed out that the change does not take place continuously as shown in Fig.5⁸⁾. The δ shows a tendency to stick to particular values and several lattice distortions with different modulation period coexist in this temperature range. Temperature change takes place by changing the density of the particular modulation.

The tetramethyl-ammonium tetrachloro-cuprate (TMA-CuCl₄)⁹⁾ shows the similar phase transitions as K₂SeO₄ (Fig.6). The INC structure is characterized by $q_1 = 0.326$ which is very close to $1/3$ and the tripled COM phase appears by the lock-in transition. However this phase is not ferroelectric as K₂SeO₄ is but is ferroelastic¹⁰⁾. The anharmonic term which couples the primary lattice distortion with strain is more dominant than the term inducing polarization.

2.3 (NH₄)₂BeF₄ and TMA - MnCl₄

AFB¹¹⁾ and TMA - MnCl₄¹²⁾ have INC phases characterized by the wave vectors which are very close to $1/2$ (Fig.7). The INC phases are very narrow in temperature range and lock in to the COM phase with $q_c = 0.5$. The COM phase is ferroelectric in AFB while it is ferroelastic in TMA - MnCl₄. The latter further transforms into another ferroelastic phase characterized by $q_c = 1/3$ which is the common low temperature phase of this kind of compounds.

2.4 TMA - MCl_4 (M : Zn, Co and Fe)

This is the group of crystals whose INC structure is very close to the quintuple superlattice. A lot of successive phase transitions take place as indicated in Fig.8: six in the Zn salt, seven in the Co salt and five in Fe salt. In the Zn salt¹³⁾ phase II is INC with the wave vector $q_1 = 0.42$ and it locks in to a COM phase with $q_C = 2/5$ which is ferroelectric. This phase is stabilized only within a narrow temperature range and it transforms into a ferroelastic monoclinic phase characterized by $q_C = 1/3$. This is isomorphous to the low temperature phase of TMA - $MnCl_4$ just mentioned above. There are two more low temperature phases but we are not interested in them here.

The Co salt¹⁴⁾ exhibits quite remarkable behavior: the INC phase locks in to the COM phase which reenters another INC phase. Except this reentrant phase the transition sequence is the same as the Zn salt.

The figure 9 shows the temperature dependence of the modulation wave vectors of both compounds¹⁵⁾. In the Zn salt the lock-in transition indicates a small jump in δ but the δ of Co salt does not show any discernible jump either at the lock-in or reentrant transitions. This is more clearly shown in Fig.10 which is the data taken by Hasebe et al.¹⁴⁾. The commensurability energy realizing this quintuple phase is likely to be very small. Actually Hasebe reported that without applying AC field he was unable to observe this change repeatedly.

The Fe salt has been studied very recently by Mashiyama and his unpublished results¹⁶⁾ indicates that the quintuple

COM phase is missing: the INC phase transforms directly into the triple ferroelastic phase.

The connection between the phases of different compounds of this kind has been beautifully made clear by Shimizu and others¹⁷⁻²⁰⁾ by measuring the pressure effect. They measured anomalies in the dielectric constants and other properties as a function of hydrostatic pressure and temperature and obtained pressure-temperature phase diagrams. The figure 11 summarizes the diagrams obtained for the three compounds. The diagram of the Zn salt¹⁷⁾ shown in (b) lacks the phase boundary line between I and II phases which was observed in later measurements¹⁸⁾. The phase II is the INC phase. The phase VII is another INC phase which only exists at high pressure. The temperature range of the COM phase III characterized by $q_c = 2/5$ becomes narrower and narrower with increasing pressure and finally disappears. This observation clearly indicates that the INC phases II and VII are continuous and constitute single phase in the two dimensional phase diagram.

They also obtained the similar diagram for the Co salt¹⁷⁾ shown in (c). By comparing this with that for the Zn salt (b) they noticed that the diagram for the Co salt is obtained from that for the Zn salt simply by shifting the origin of the pressure axis. This explains how the INC phase in the Co salt is reentrant. The similar was the case for the Fe (Fig.11(a)) and Mn salts^{19,20)}. Then the P-T diagrams for various compounds can be put together into a single diagram shown in Fig.12, in which the origin of pressure is different for each compound as shown by the arrows. In order to reproduce each

diagram completely it is necessary to change the scale of both axes by the units shown by segments in the figure. Now we realize how the quintuple ferroelectric phase is missing in the Fe and Mn salt at normal pressure. It is existing at high pressure but missing at normal pressure.

As was observed by Mashiyama and Tanisaki¹²⁾ the INC phase in the Mn salt is very narrow and there is another phase with $q_C = 1/2$ prior to entering the common low-temperature phase. Therefore there must be a phase boundary which separates the INC phase II from the COM phase with $q_C = 1/2$. The correct diagram is supposed to be the one shown in Fig.13 which is a private communication to the author from Mashiyama.

It is interesting to combine this results with the diffraction measurements and to speculate how the modulation wave vector changes within the INC area. The dotted lines in Fig.13 show the contours of equal q value composed from the diffraction results. The wave vector becomes smaller with increasing pressure or decreasing temperature. In the left-hand side of the area the q value is larger than $2/5$ and in the right-hand side it is smaller than $2/5$. We can now understand the nature of the quintuple ferroelectric phase which appears in the vicinity of the boundary which separates the high q and low q areas. This is just a transitory phase within a wide INC area. The COM phase comes into existence when the INC wave vector happens to approach the COM value of $2/5$ and is clamped there. However the commensurability energy is so small that the crystals are commensurate only within a very small area and above the round tip of the phase boundary it

does not clamp the wave vector any more at the COM position though it passes through the COM value.

2.5 Other TMA salts

Deuterated compound of TMA-ZnCl₄ exhibits quite a different behavior compared with the undeuterated compound mentioned in the preceding subsection. One sample examined indicates coexistence of a COM phase ($q_c = 1/2$) with the INC phase²¹⁾. Later investigation has disclosed that the COM phase exists at a small but finite value of applied stress X_4 ²²⁾. The coexisting COM phase is then interpreted as the one induced around imperfections of the crystal by residual stress.

Recently TMA-CuBr₄ was studied and it has been reported that in the COM phase the spontaneous polarization appears along the c direction²³⁾. This is quite exceptional in the K₂SeO₄ family. A preliminary X-ray measurement²⁴⁾ indicates that the modulation is found for the first time along the b axis.

3. UNDERSTANDING THE INC INSTABILITY FROM LATTICE-DYNAMICAL POINT OF VIEW

Now so much for the details of the INC insulators of the K₂SeO₄ family, let us consider them from somewhat general point of view. The origin of the INC instability in this kind of crystals is not so well understood as in the cases of the low-dimensional conductors. The interionic forces acting

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3. UNDERSTANDING THE INC INSTABILITY FROM LATTICE-DYNAMICAL POINT OF VIEW

Now so much for the details of the INC insulators of the K₂SeO₄ family, let us consider them from somewhat general point of view. The origin of the INC instability in this kind of crystals is not so well understood as in the cases of the low-dimensional conductors. The interionic forces acting

among the constituents are quite complicated and only one can make a remark that an instability at a general wave vector is the result of complicated competition and cancellation among the forces of various ranges.

Experimentally this has been demonstrated by measuring the dispersion relation of the unstable phonon in K_2SeO_4 ¹⁾. The figure 14 shows the energy-wave vector relations of the phonons propagating in the modulation direction. The relation is shown in the extended zone scheme, that is, the right half is an unfolded part of the optic branch. It should be noticed that this extended zone scheme is not just a convention but it indicates the true periodicity of the lattice vibrations propagating in the c^* direction because of the existence of the c glide in the structure. The dispersion relation shows a remarkable temperature-dependence, or softening, and the condensation of the soft phonon takes place at an INC point in the vicinity of $1/3$. We can apply the Fourier analysis on these curves and obtain effective force constants between atomic layers lying perpendicularly to the wave vector. The minimum distance between the layers is $c/2$. The solid curve is the result of the fitting. The interlayer force constants obtained by the analysis are shown in Fig.15 as functions of temperature. By this analysis¹⁾ it was made clear that the third neighbor interlayer forces are dominant over the first and second neighbor forces and the collapse of the latter causes the instability in the vicinity of $2/3$.

Theoretically it has been suggested by Haque and others²⁵⁾ that the instability is the result of competition between

Coulomb dipolar and short-range repulsive forces.

Although the similar investigations have not been made for the other kind of crystals, it is natural to assume that the similar kind of lattice instability takes place also in other crystals of this family. Also it is quite likely that details of the competition among forces of various ranges are different from one substances to another causing the instability at a different wave vector of the extended zone.

In this respect it is interesting to see the position where the instability takes place for each substance. The figure 16 summarizes the INC and COM positions of the wave vectors on the c^* axis of the extended zone. The open circles indicate the INC wave vectors at T_1 and the horizontal arrows indicate the change of the INC wave vectors within the INC phases and solid circles or triangles show the COM wave vectors characterizing the successive COM phases. The circles are used for the ferroelectric phases and the triangles for the ferroelastic phases. It is important to distinguish the wave vectors $2/3$ from $1/3$, though they are identical point in the reduced zone scheme. Mere $1/3$ is the Σ_3 mode at the same position in the reduced zone while Σ_2 mode at $1/3$ in the reduced zone corresponds to the mode at $2/3$ in the extended zone. In the extended zone it is unnecessary to distinguish the Σ_2 mode from the Σ_3 mode. The mode nature is continuous.

The figure has shown that the instability takes place at various scattered points from $1/3$ to $2/3$. This implies that a particular lattice dynamical mode in which the constituents in one layer oscillate with a certain phase difference from

those in the neighboring layers has a relatively low energy and becomes unstable. The phase difference is neither zero (in phase) nor π (antiphase).

From the symmetry point of view the appearance of the INC structure as a result of a phase transition is related to the Lifshitz condition as was mentioned in the introduction. In the lattice-dynamical language it means the zero gradient of a dispersion surface. In the present crystal symmetry there is no symmetry requirement for the zero gradient at any particular commensurate wave vector in the extended zone including the midpoint which is the zone boundary of the reduced zone. Therefore once the lattice instability occurs somewhere on the extended axis the crystal structure does not particularly favor the COM wave to freeze in. The tendency for the crystal structure to become unstable somewhere on this wide extended axis together with the lack of the symmetry restriction for a COM structure constitutes the general reason why this family of structure is rich in the INC phase transitions.

The commensurability energy is provided through a higher order anharmonic interaction. The difference of the wave vectors of the COM phases is the result of the difference of the orders of the predominant anharmonic interaction. This causes another variety in the family. The table 1 shows the order of the anharmonic terms and the nature of the induced macroscopic quantities of various compounds.

In summary 1) we reviewed the INC phase transitions in the K_2SeO_4 family of crystals and 2) we pointed out the wide

variety of the INC phase transitions is attributable to the lattice instability of the same origin; only the wave vector of the instability is different.

Acknowledgement

The author wishes to thank Dr. H. Mashiyama for the communication of unpublished information. The neutron scattering measurements at Tokai have been carried out in collaboration with Dr. K. Gesi. The author is grateful to him for the collaboration and helpful discussion.

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References

- (1) Iizumi, M., Axe, J.D., Shirane, G. and Shimaoka, K.: Phys. Rev. B 15, 4392 (1977).
- (2) Levanyuk, A.P. and Sannikov, D.G.: Sov. Phys. Solid State 18, 245 (1976).
- (3) Gesi, K. and Iizumi, M.: J. Phys. Soc. Jpn. 48, 697 (1980).
- (4) Iizumi, M. and Gesi, K.: J. Phys. Soc. Jpn. 45, 711 (1978).
- (5) Iizumi, M. and Gesi, K.: J. Phys. Soc. Jpn. 49 Suppl. B (Proc. JSSF-2, Kyoto, 1980) 72 (1980).
- (6) Gesi, K. and Iizumi, M.: J. Phys. Soc. Jpn. 46, 697 (1979).
- (7) Gesi, K. and Iizumi, M.: J. Phys. Soc. Jpn. 45, 1777 (1978).
- (8) Iizumi, M. and Gesi, K.: unpublished.
- (9) Gesi, K. and Iizumi, M.: J. Phys. Soc. Jpn. 48, 1775 (1980).
- (10) Sawada, A., Sugiyama, J., Wada, M. and Ishibashi, Y.: J. Phys. Soc. Jpn. 48, 1773 (1980).
- (11) Iizumi, M. and Gesi, K.: Solid St. Commun. 22, 37 (1977).
- (12) Mashiyama, H. and Tanisaki, S.: J. Phys. Soc. Jpn. 50, 1413 (1981).
- (13) Tanisaki, S. and Mashiyama, H.: J. Phys. Soc. Jpn. 48, 339 (1980).
- (14) Hasebe, K., Mashiyama, H. and Tanisaki, S.: J. Phys. Soc. Jpn. 49, 1633 (1980).

- (15) Mashiyama, H., Hasebe, K. and Tanisaki, S.: J. Phys. Soc. Jpn. Suppl. B (Proc. JSSF-2, Kyoto, 1980) 92 (1980).
- (16) Mashiyama, H.: private communication.
- (17) Shimizu, H., Oguri, A., Abe, N., Yasuda, N., Fujimoto, S., Sawada, S., Shiroishi, Y. and Takashige, M.: Solid St. Commun. 29, 125 (1979).
- (18) Shimizu, H., Kokubo, N., Yasuda, N. and Fujimoto, S.: J. Phys. Soc. Jpn. 49, 223 (1980).
- (19) Shimizu, H., Abe, N., Yasuda, N., Fujimoto, S., Sawada, S. and Shiroishi, Y.: Jpn. J. Appl. Phys. 18, 857 (1979).
- (20) Shimizu, H., Abe, N., Kokubo, N., Yasuda, N., Fujimoto, S., Yamaguchi, T. and Sawada, S.: Solid St. Commun. 34, 363 (1980).
- (21) Gesi, K. and Iizumi, M.: unpublished.
- (22) Mashiyama, H., Tanisaki, S. and Gesi, K.: J. Phys. Soc. Jpn. 50, 1415 (1981).
- (23) Wada, M., Suzuki, M., Sawada, A., Ishibashi, Y. and Gesi, K.: J. Phys. Soc. Jpn. 50, 1813 (1981).
- (24) Mashiyama, H.: private communication.
- (25) Haque, M.S. and Hardy, J.R.: Phys. Rev. B 21, 245 (1980).

Table 1 Classification of the induced macroscopic quantities in COM phases in the crystals of the K_2SeO_4 type. Components of the spontaneous polarization in the ferroelectric cases and the unique axes of the ferroelastic cases are indicated in the parentheses.

g_c	FERRO-ELECTRIC	FERRO-ELASTIC
$\frac{1}{2}$	$(ND_4)_2BEF_4$ (P_Y)	TMA-MnCl ₄ (a)
$\frac{2}{3}$	K_2SeO_4 RB_2ZnCl_4 RB_2ZnBr_4 K_2ZnCl_4 (P_X)	TMA-CuCl ₄ (b)
$\frac{1}{3}$		TMA-MCl ₄ M: Zn, Mn, Fe & Co (c)
$\frac{2}{5}$	TMA-MCl ₄ M: Zn & Co (P_X)	

(MONCL. UNIQUE AXIS)

? TMA-CuBr₄ (P_Z)

TMA : $\{N(CH_3)_4\}_2$

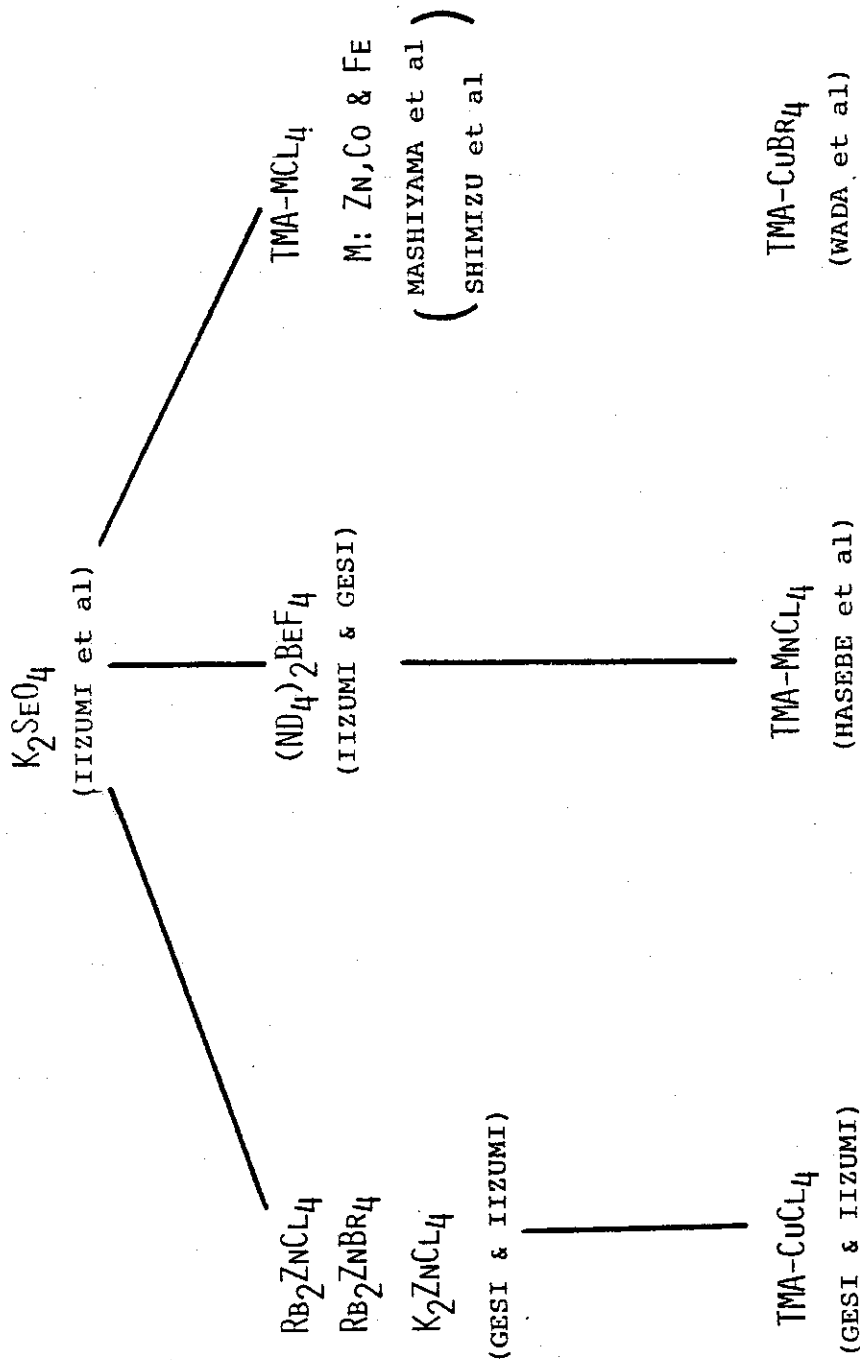


Fig. 1 Classification of the crystals belonging to the K_2SeO_4 type. Names in parentheses show authors of the representative references.

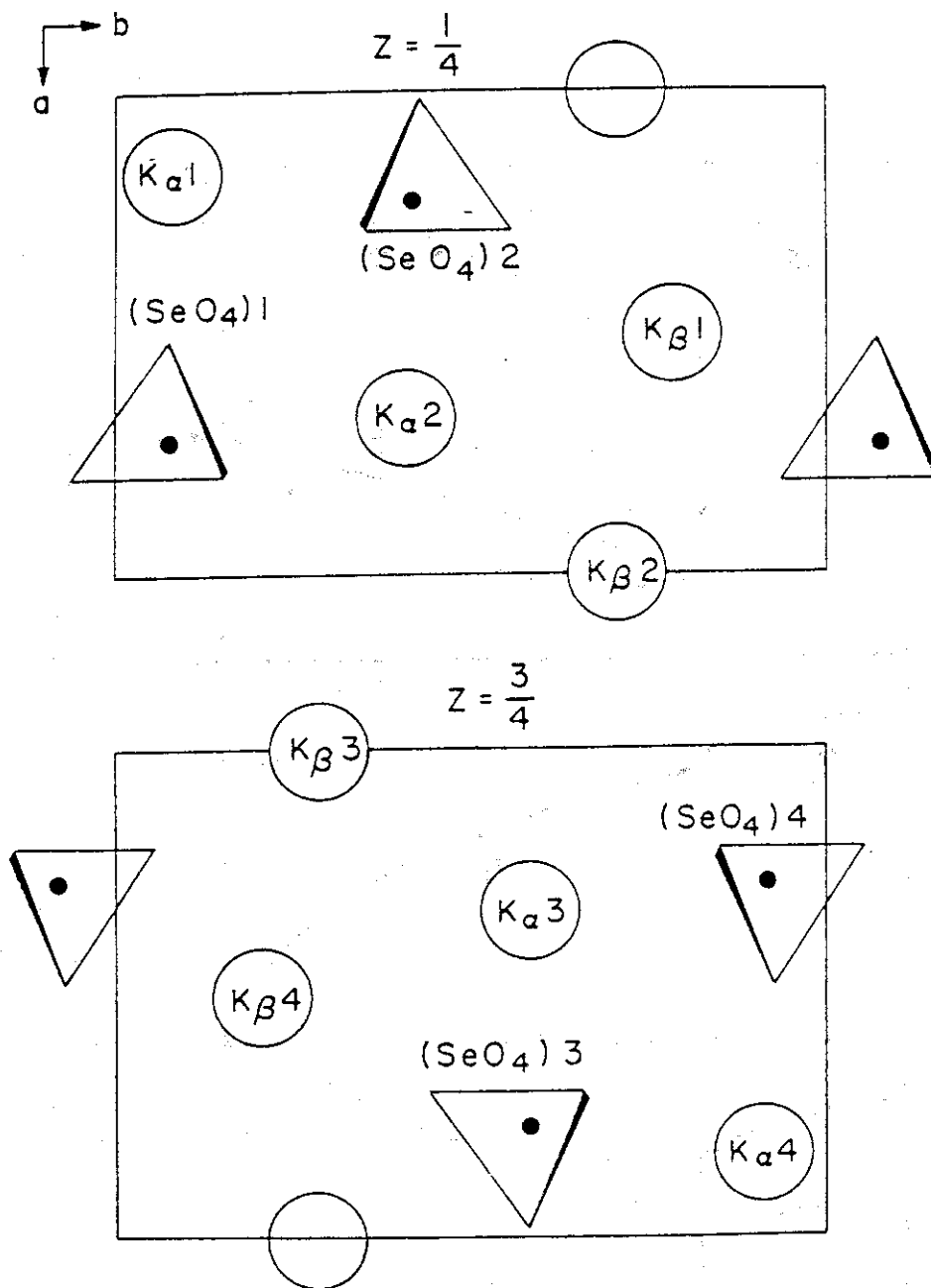


Fig. 2 Schematic crystal structure of K_2SeO_4 . The SeO_4 groups form nearly regular tetrahedra which are indicated by triangles in this figure.

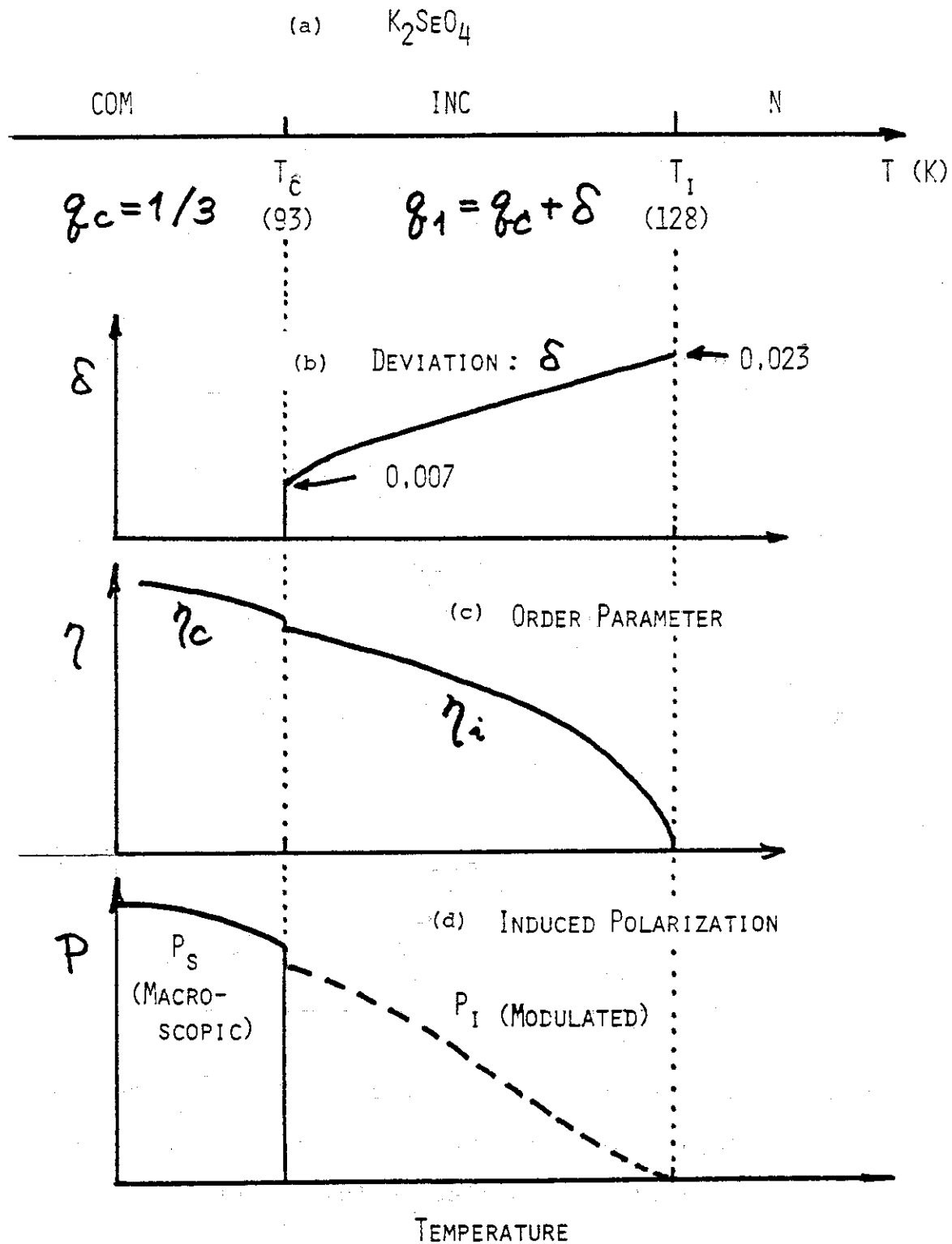


Fig. 3 Phase transitions and temperature change of essential physical quantities in K_2SeO_4 .

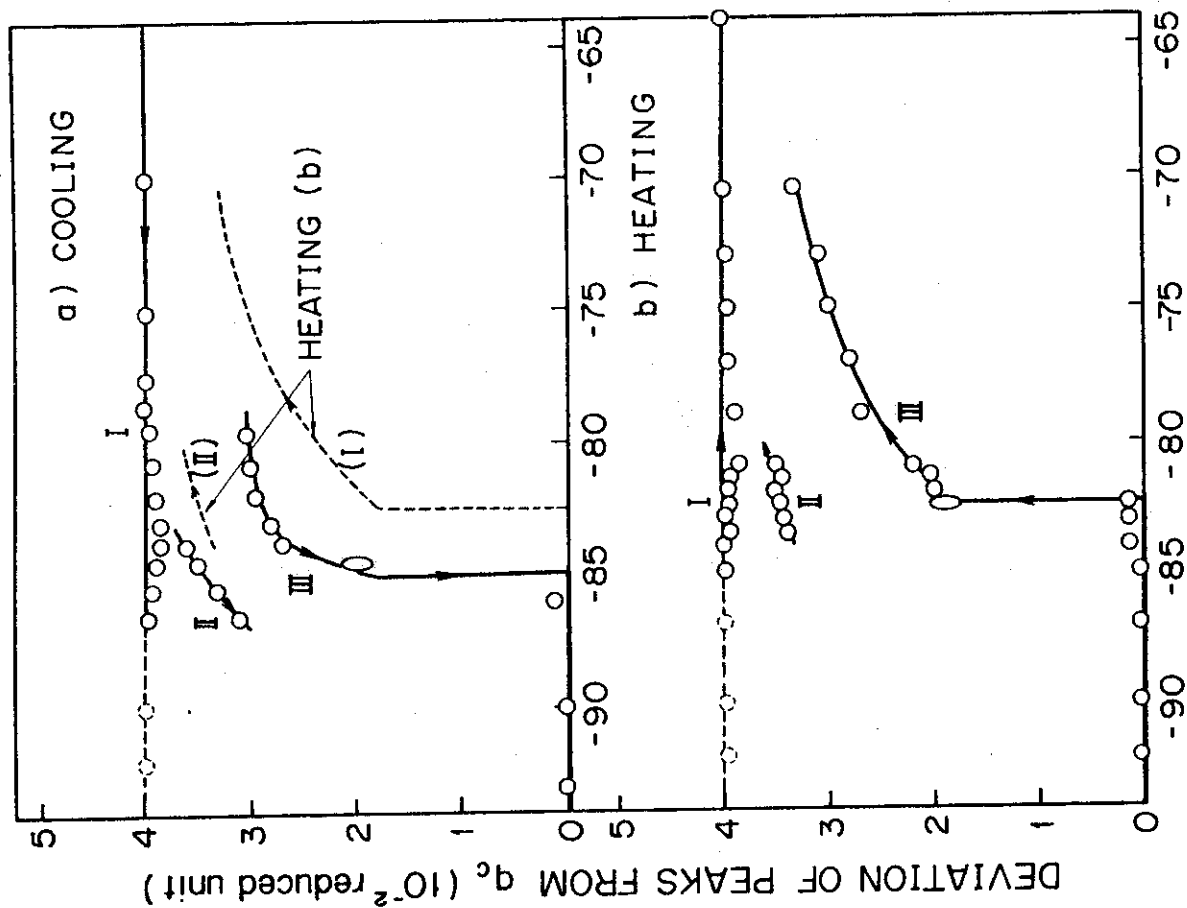


Fig.5 Details of the temperature change of the satellite position in Rb_2ZnBr_4 .

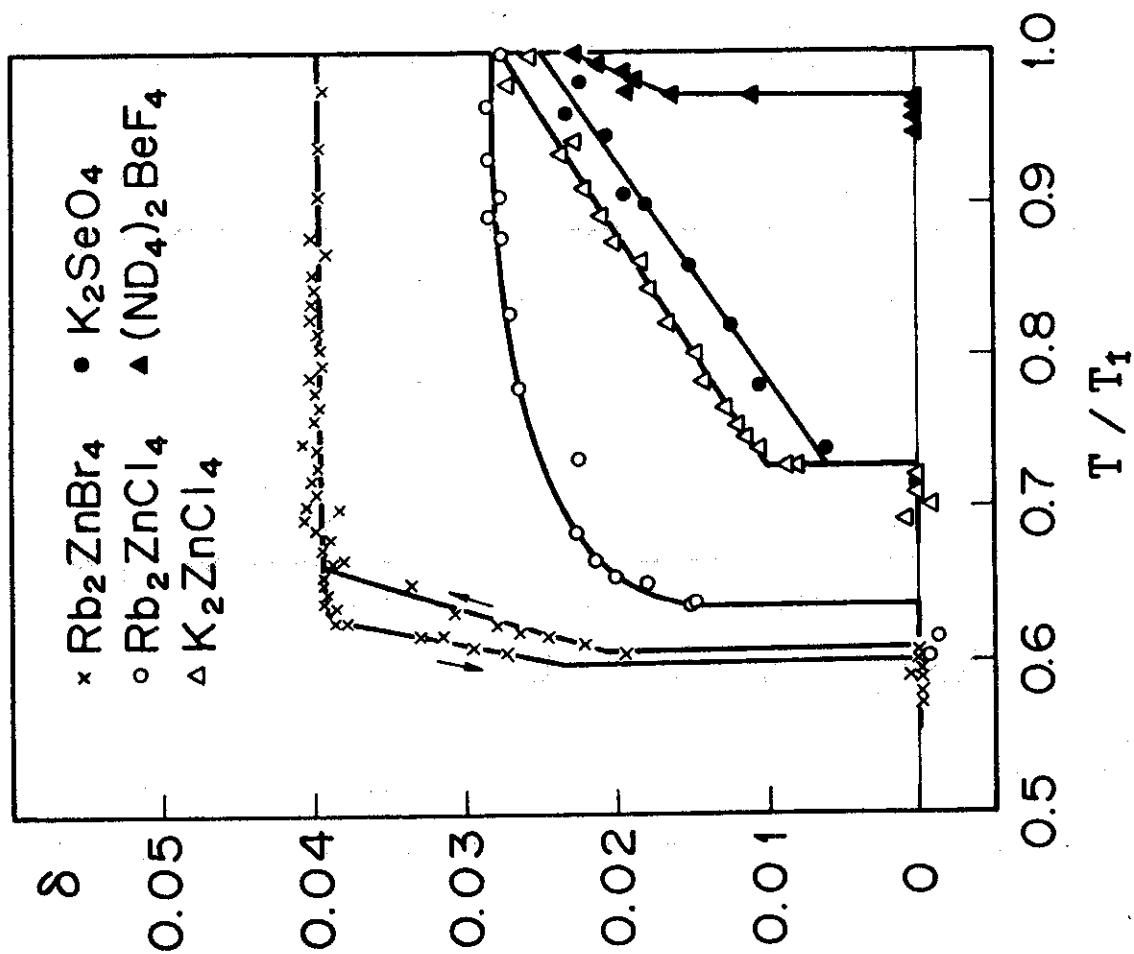


Fig.4 Temperature change of the deviation parameter δ of Rb_2ZnCl_4 and related crystals.

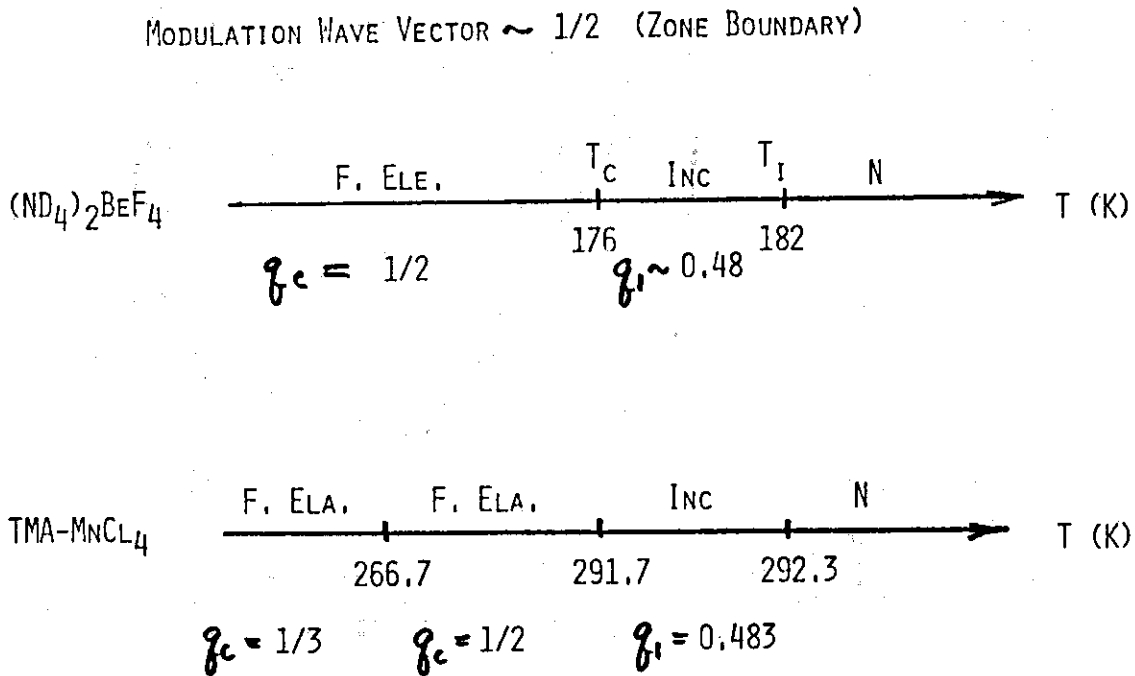
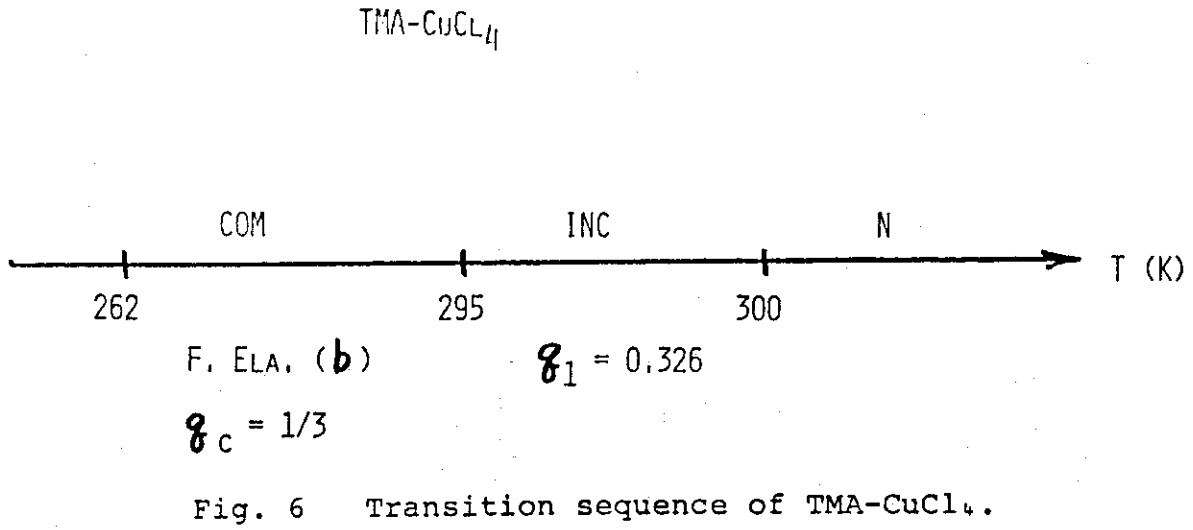
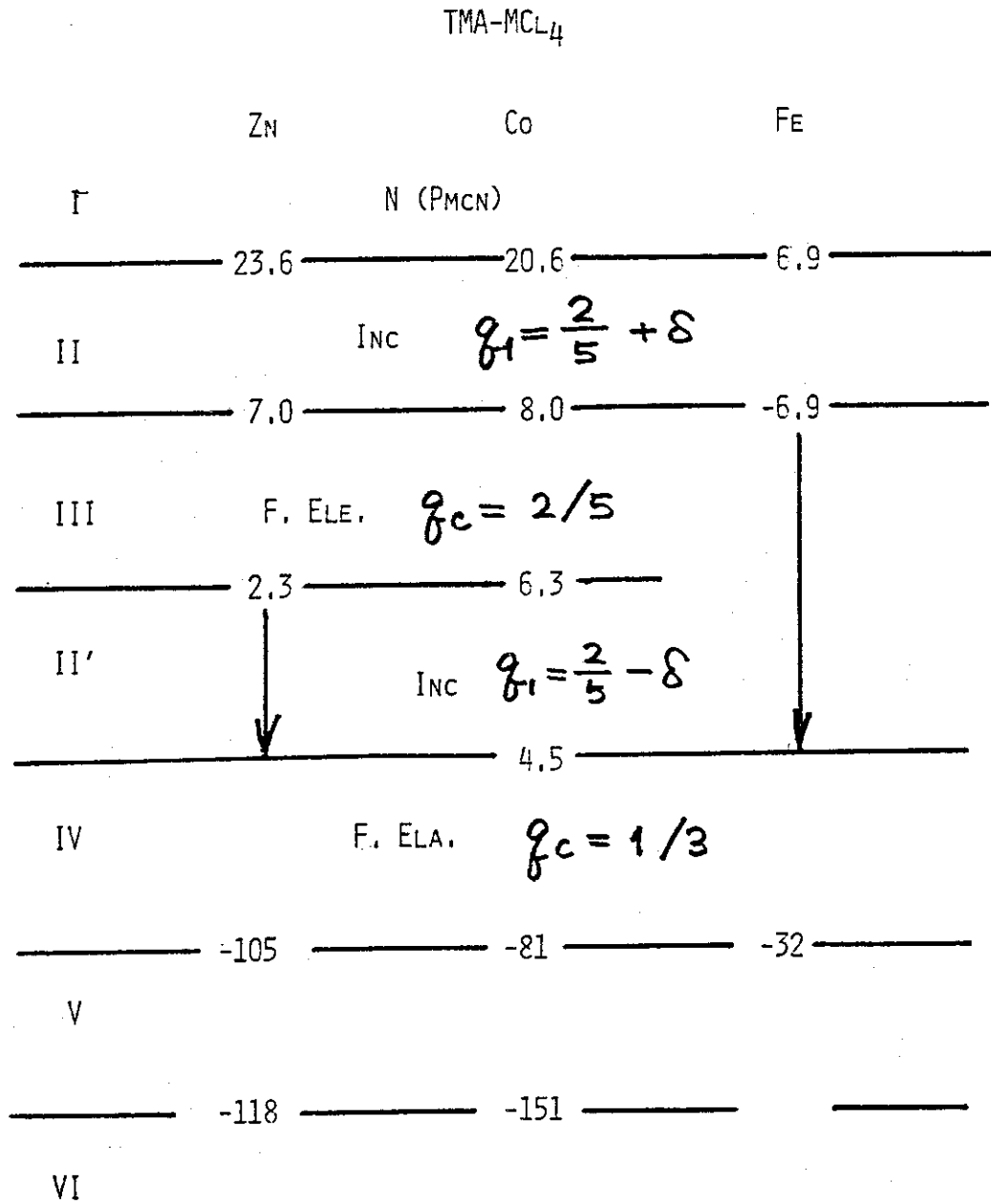


Fig. 7 Transition sequences of the crystals, INC phases of which are characterized by wave vector close to 1/2.



NUMBER: TRANSITION TEMPERATURE (°C)

Fig. 8 Transition sequences of TMA-MCl₄ (M : Zn, Co and Fe).

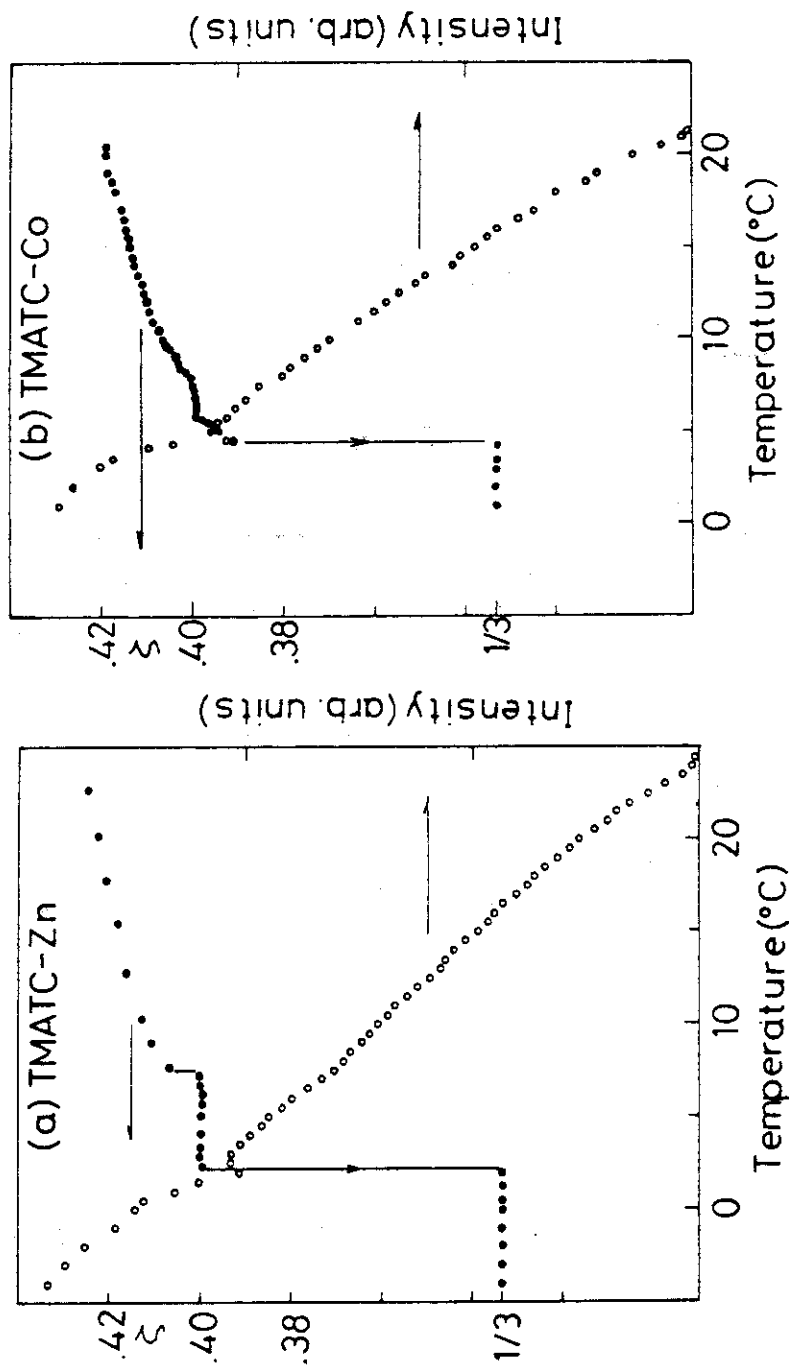


Fig. 9 Positions and intensities of satellites in

TMA-MCl₄ (M: Zn and Co).

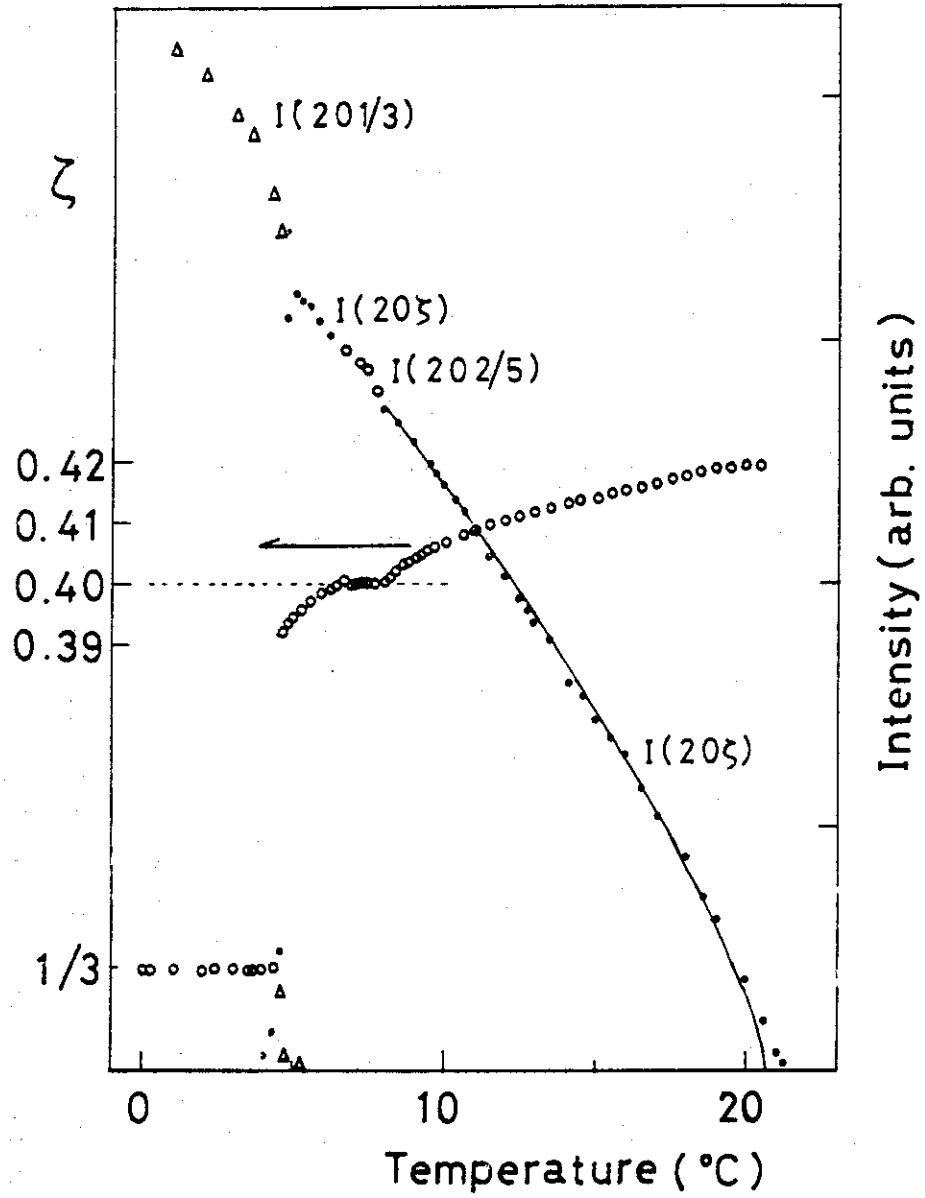


Fig.10 Temperature change of the modulation wave vector ζ of TMA-CoCl₄. The change of satellite intensity is also shown.

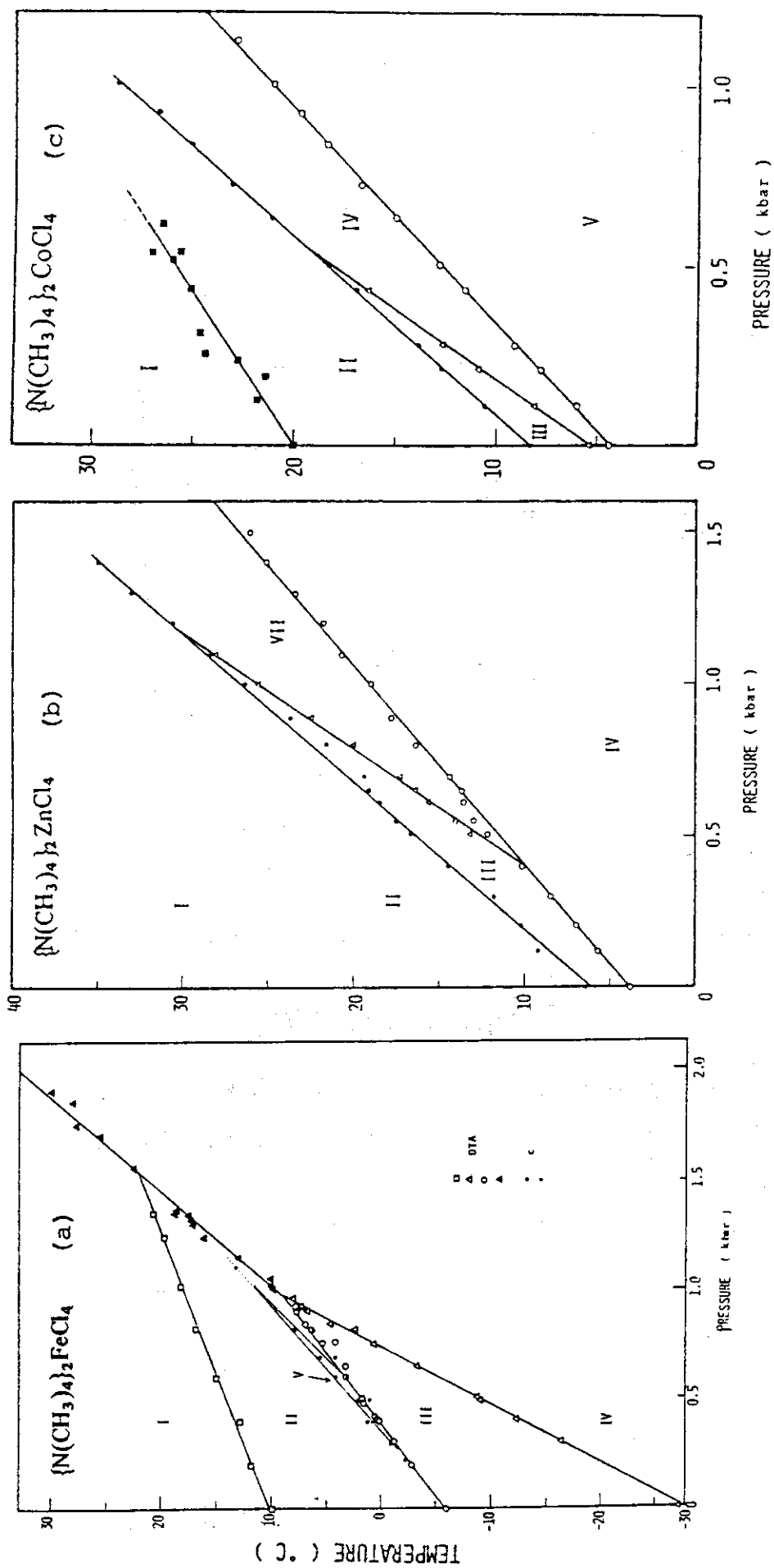


Fig.11 Pressure-temperature phase diagram of TMA-MCl₄

(M : Fe(a), Zn(b) and Co(c)).

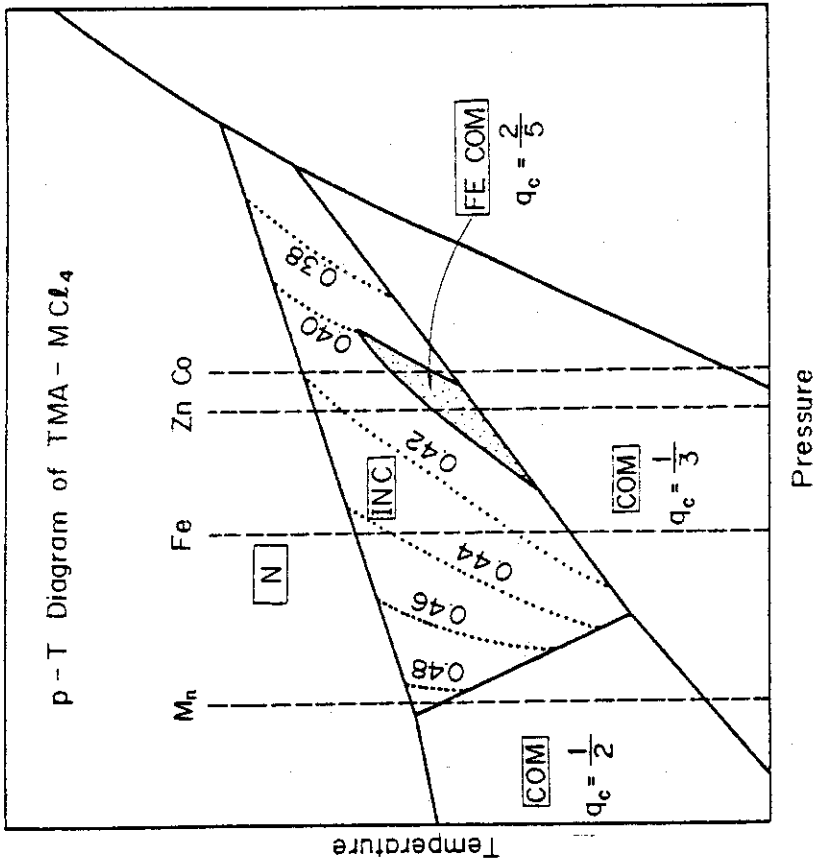


Fig.13 The p-T phase diagram corrected for the COM phase with $q_c = 1/2$ in the Mn salt. The dotted lines in the INC area indicate contours of equal modulation wave vectors which are estimated from the temperature change of the modulation wave vectors of each compounds at zero-pressure.

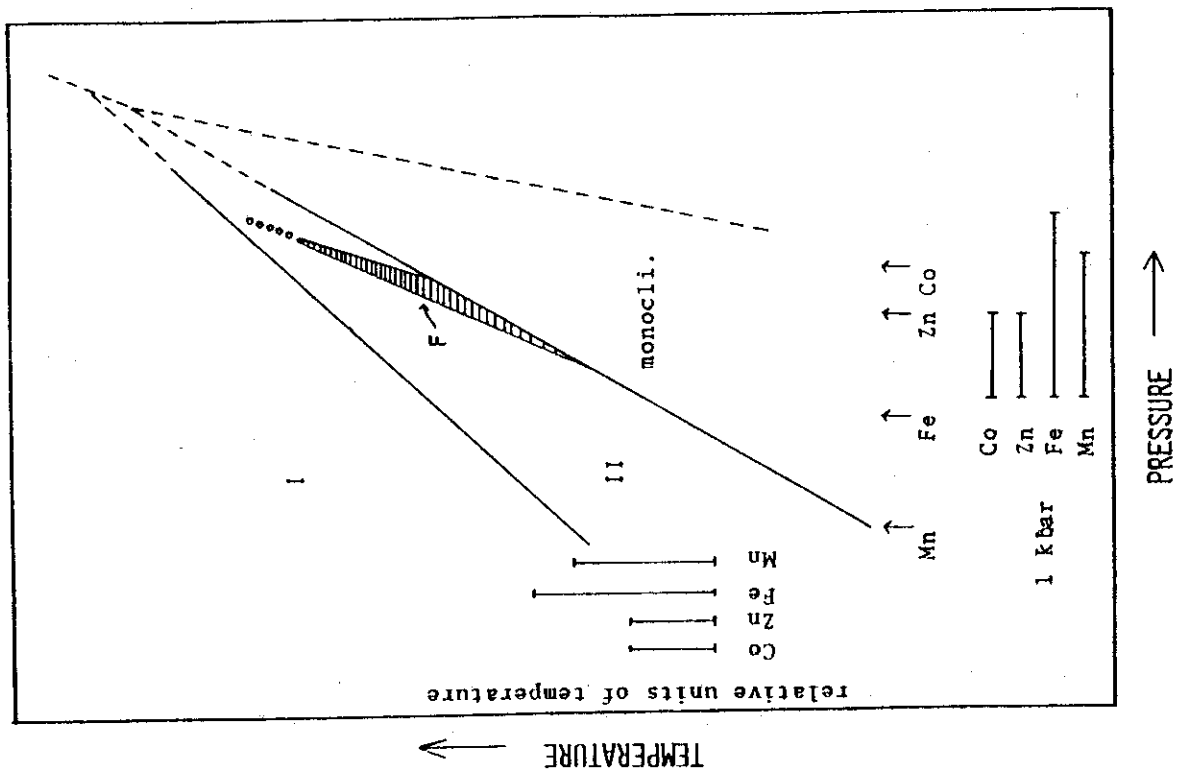


Fig.12 Schematic phase diagram of TMA-MCl₄. Arrows with the element names indicate the zero-pressure point for each compounds. Relative units of the temperature and pressure axes are shown by bars along the axes.

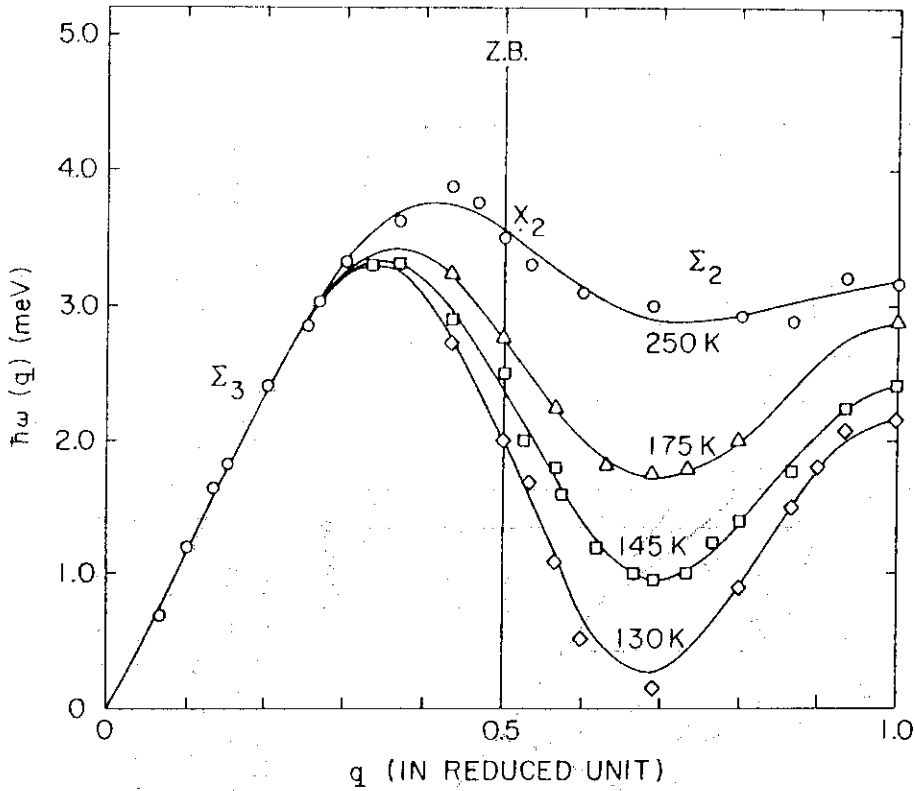


Fig.14 Dispersion relation of a transverse acoustic mode in K_2SeO_4 , propagating in the direction in which the modulation takes place below $T_i = 128$ K. The dispersion relation is shown in the extended zone scheme.

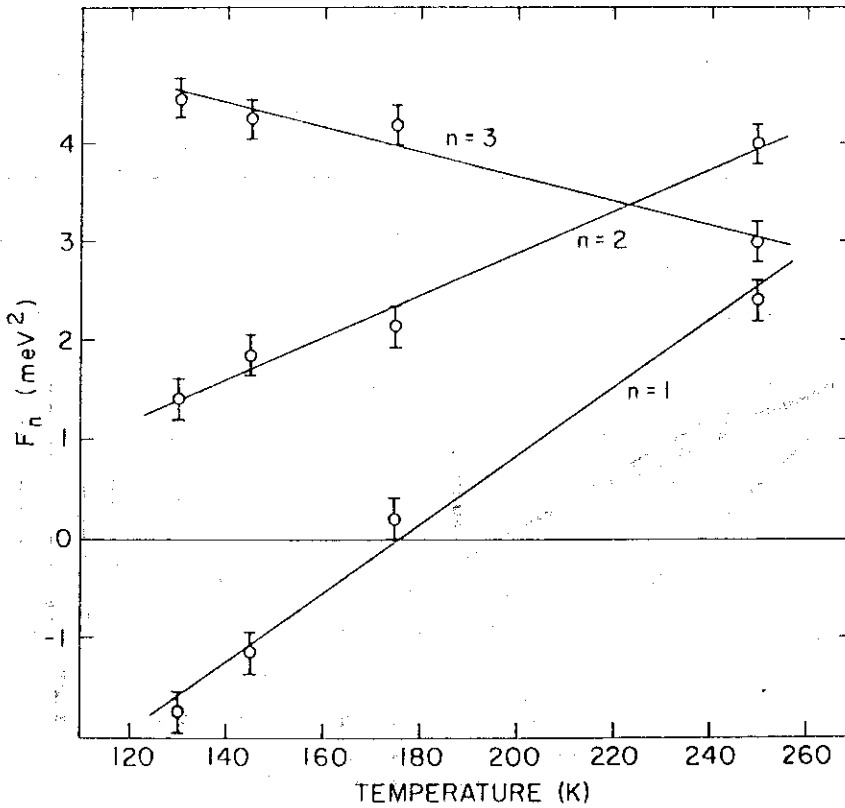


Fig.15 Temperature change of the effective interlayer force constants of different ranges in K_2SeO_4 .

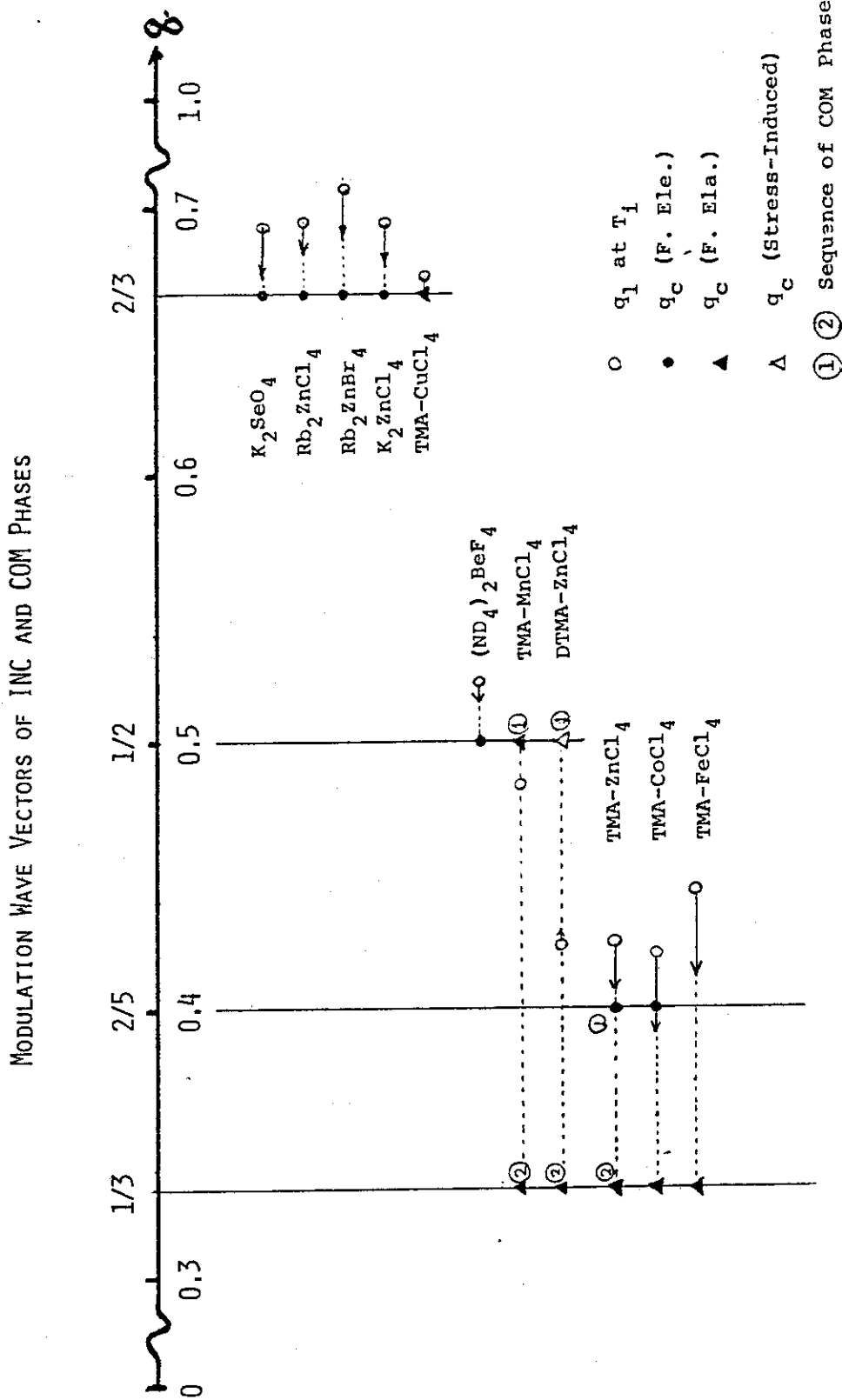


Fig.16. Compilation of the INC and COM positions of the modulation wave vector in crystals belonging to the K_2SeO_4 type. Positions are shown in the extended zone by the symbols indicated in the figure.