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論　文

Heat Capacity Measurements Around Incommensurate-Normal Phase Transition of Synthetic Åkermanite Solid Solutions and the Transition Entropies

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Åkermanite solid solution is known as a mineral showing incommensurate to normal (I-N) phase transition at a temperature between 80 and 250℃, which depends on the chemical composition in the substitution series. To clarify the thermal behavior around the transition temperatures, crystals with various chemical compositions were synthesized by the floating zone method and the heat capacities above room temperature were measured by means of a small scale adiabatic calorimeter, using less than 2g of a sample for each measurement. The obtained I-N transition entropy values, about 1.7 $JK^{-1}mol^{-1}$ in average, are almost the same, independent of composition and the transition temperature. The transition mechanisms and the value of transition entropy are discussed in terms of a statistical model related to the modulated structure.

Introduction

Åkermanite is the mineral name of an end member of a solid solution series between åkermanite ($Ca_2MgSi_2O_7$) and gehlenite ($CaAl[AlSiO_7]$). The mineral occurs naturally containing appreciable amounts of both Na and Fe. Melilite has been used as the group name of the solid solution series. In 1986, Hemingway *et al.*[1] reported the heat capacities of a synthetic akermanite sample ($Ca_2MgSi_2O_7$) measured by low temperature adiabatic calorimetry in a temperature range between 9 to 374K and by the DSC method between 369-995K. They also gave smoothed analytical expressions for thermodynamic functions of the mineral which were derived by using the calorimetric data of their own and those from the literature. They found a sharp anomaly in heat capacity at 357.9K and an abnormal bending at 693K in thermal expansion without any DSC-heat effect. The single crystal X-ray diffraction patterns and the electron diffraction patterns showed a set of weak satellite reflections which suggested the existence of an incommensurate phase due to local displacements of the calcium ions and accompanying distortion of the $[MgSi_2O_7]^{2-}$ framework. Seifert *et al.*[2] studied independently the incommensurate phase with a set of rectangular modulations of a wavelength of about 19Å in the [110] direction in synthetic $Ca_2Mg_{1-x}Fe_xSi_2O_7$ (x=0.0-0.7). The I-N transition temperature of the substitution series migrates from 80℃ at x=0.0 to 250℃ at x=0.6. Iishi *et al.*[3),4)] showed that the $Ca_2Mg_{1-x}Co_xSi_2O_7$ phase also has the same type of incommensurate phases as those found in the Mg-Fe series of åkermanite. Recently Hagiya *et al.*[5),6)] gave a modulation structure model based on X-ray single crystal diffraction analysis.

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In the present work, the various kinds of substitution series of åkermanite have been synthesized. A small scale adiabatic calorimeter[7] was used to determine the heat capacities from room temperature to 600℃[8]. The small scale of the calorimeter enables evaluation not only in the intermittent measurement as a conventional mode but also in the continuous heating mode especially around the phase transition temperature. The latter mode of measurement was made possible by miniaturization of the calorimeter which contributed to the precise determination of heat capacity profiles around the transition temperature.

Specific heat capacity was used through the present work to represent heat capacity-value, because it is convenient to compare graphically with one another materials with various formula weights in the substitution series.

Samples

Heat capacity of NBS SRM-720 sapphire was measured for calibrating absolute values. Fine crystal of quartz from Brazil, cylindrically shaped 2.2444g, was used to evaluate the continuous heating method of the calorimeter, especially around phase transition at 573℃.

Crystals of the åkermanite substitution series were prepared by the floating zone method or by a conventional sintering method[2]. The weight of a synthesized crystal is about 2-3g, which is suitable for such a small scale calorimeter used in precise heat capacity measurement. For the calorimetric measurements, each rod of as-grown crystal was crushed to fragments a few millimeters in size suitable for the sample vessel of the calorimeter. The total amount of fragments, used for each measuremnet was 1.8-2g. The chemical compositions of synthesized compounds are shown in Table 1.

Table 1 Compositions, entropy values and transition temperatures for IN-N transition of various solid solution series of synthetic åkermanite.

Formula	Comp.	ΔS_t/ $JK^{-1}mol^{-1}$	θ/℃
$Ca_2Mg_{1-x}Co_xSi_2O_7$	x=0.00	1.57	83-84
	0.01	1.86	85
	0.20	1.56	113
	0.40	1.74	143
	0.50	1.91	160
	0.60	1.75	171
	0.80	1.75	195
	1.00	1.71	220
$Ca_2Co_{1-x}Fe_xSi_2O_7$	x=0.01	1.63	218
	0.05	1.67	213
	0.10	*	
$(Ca_{1-x}Sr_x)_2CoSi_2O_7$	x=0.04	1.92	202
	0.10	1.66	169
	0.20	*	
	0.30	*	
$Ca_2Mg_{1-x}Zn_xSi_2O_7$	x=0.20	1.77	91
	0.40	1.62	101-102
	0.60	1.84	113
	0.80	1.68	122
	1.00	1.64	130
Average ΔS_t		1.72	

* Entropy value dose not determined due to diffusing of the Cp-θ profile.

Experimental

Method of calorimetric measurement

Details on the adiabatic calorimeter used were described[7]. Electric power for heating, the heating duration and the sample temperature were measured and recorded by a data acquisition system equipped with a microcomputer. The temperature was measured by two sets of CA-thermocouples of sheath type (*o.d.*=0.5mm), connected in series and inserted at the center of the sample vessel made of Pt/10% Rh alloy. The electromotive force was measured by means of a digital voltmeter (YHP 751, 6.5 digits). The voltage to temperature conversion was performed based on the IPTS-68. The conventional intermittent heating mode of measurement applied in the normal heat capacity region, and the continuous heating mode was adopted for the temperature range around heat capacity-anomalies.

Intermittent heating mode of measurement

The heat capacity at a temperature was measured in the mode as an average in a temperature width of about 2.5K. The heat capacities of the empty calorimeter were determined repeatedly from room temperature to 600℃ by this method. The whole 295 points obtained from seven

indenpendent measurements are used for calculation of the heat capacity. The data were smoothed in terms of six sets of second order equations determined in each of the temperature divisions, because any one of polynomial equations tested was insufficient to simulate the whole range due to the delicate curvature. The deviation of each datum from the smoothed value was less than 0.5%. Sapphire (α-Al_2O_3, NBS SRM-720) samples (1.8-2g) were used for the heat capacity measurements to evaluate the accuracy and precision. The measured heat capacities gave systematic deviation larger by about 4% than those of the recommended values by NBS. This indicates a systematic deviation between the measured electric power and the real energy supplied to the sample. The main cause would come from the sites of the lead-wire/heater connection, that is, the deviation from the ideal connection due to the difficulty of construction of the small calorimeter. The systematic deviation plot was evaluated with a second order equation as the supplied electric power correction in the whole temperature range from room temperature to 600℃, hence this could be corrected. After the correction, the measured specific heat capacities of sapphire and the NBS recommended values[9] are shown in Fig.1. Fig.2 shows the deviation plots after the correction. The whole date are plotted within ±1% deviation and 80% of the plots within ±0.5%.

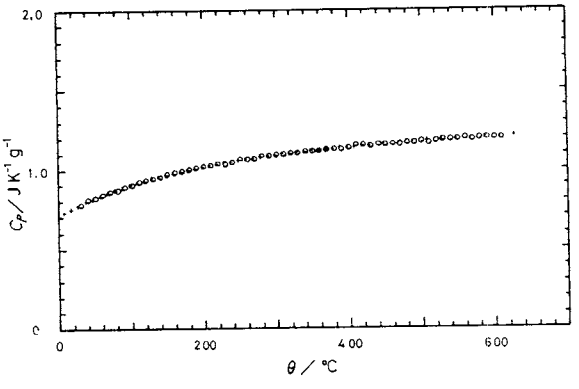

Fig.1 Specific heat capacity of sapphire, NBS SRM-720, measured by the intermittent heating method. circle: this work, cross: NBS recommended value[9].

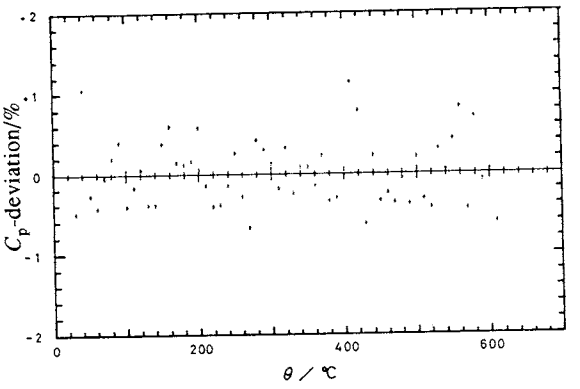

Fig.2 Deviation percent plot for specific heat capacities of NBS sapphire, deviation % = $100\times[Cp_{obs}(\theta)-Cp_{NBS}(\theta)]/Cp_{NBS}(\theta)$.

Heat exchange correction for the continuous heating mode of measurement

The present calorimeter is characterized by its small scale: heat capacity of the empty calorimeter, 3.2JK^{-1} at 30℃, with internal volume of the sample container of 2.6cm^3 in which about 1.8-2g of a silicate sample, for example, is loaded. The heat balance in a practical adiabatic calorimeter system is expressed as for a sample loading:

$$[Cp(T)m + C(T)]\, d\theta = [Pw(T) + L(T)]\, dt \quad (1)$$

where $Cp(T)$: specific heat capacity of the sample at a temperature T; m=sample weight; $C(T)$=heat capacity of the empty calorimeter; $d\theta$=temperature elevation; $Pw(T)$=supplied electric power; $L(T)$=heat exchange between the central part and the adiabatic shield; dt=heating duration for the temperature elevation by dT. The heat exchange, $L(T)$, is unavoidable and should be corrected in the continuous heating measurement, even if the calorimeter preserves good adiabatic condition during the measurement. The correction was performed as follows. The first term of the equation (1), $[Cp(T)m + C(T)]$ the heat capacity of the calorimeter with sample, can be measured precisely and directly by the intermittent heating method with the one and the same sample as that used in the continuous heating measurement. Then the sample must be stable enough during repeated measurements. Åkermanite samples were proved to stand unchanged after

heating up to at least 600℃.

Rewriting the equation (1), we obtain the heat exchange;

$$L(T) = [Cp(T)m + C(T)]\ dT/dt - Pw(T) \qquad (2)$$

where dT/dt is the heating rate in the continuous heating measurement. Data sets such as the time, the temperature, the heating rate and the supplied electric power $Pw(T)$ were measured at 5s-intervals in successive data acquisition cycles of the continuous heating method.

An example for the heat exchange value versus temperature is shown in Fig.3a for near transition temperature range measured with quartz from Brazil. Except for the range around the transition, the plot maintains a smooth and monotonous bending as seen in the figure, so that we can simulate the data with a polynomial equation in the whole temperature range measured for correcting the heat exchange. The calculated curve with a 6th-order equation simulates well the heat exchange (Fig.3b). We can also assume reasonably that the same equation is applicable to interpolate the heat capacities even in the heat capacity anomaly at the transition range. The results of the heat capacity measurement of quartz after the correction are shown in Fig.4 as the final results in combination of the intermittent heating method in the normal heat capacity region with the continuous heating method near transition anomaly region. The recommended heat capacity values[10] are also plotted in the same figure.

Method of calculation of transition entropies

As we did not have suitable models for the lattice-phonon heat capacity to obtain transition entropies of the solid solution series, the background heat capacities were evaluateded in a conventional way by connecting two points selected visually at both sides of a transition peak in the specific heat capacity-temperature plots. The temperature width ranges almost from 20K to 40K for the individual integration in most cases, but for example exceeds

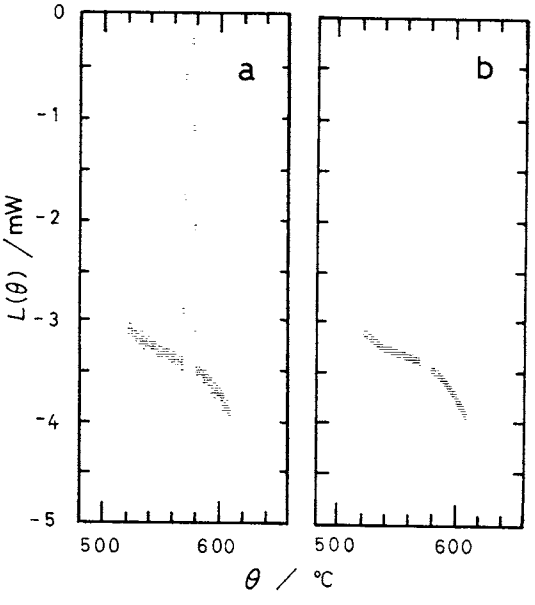

Fig.3 Heat exchange, L(θ), plot for specific heat capacity measurement of quartz(2.2444g) from Brazil, obtained from the continuous heating method (supplied electric power 44mW) and the intermittent heating method. a: measured heat exchange value vs. θ plot near transition temperature. Dispersed values indicate large difference between specific heat capacities obtained from the two methods in the transition anomaly region, b : plot for the fitted values with the 6th-order equation.

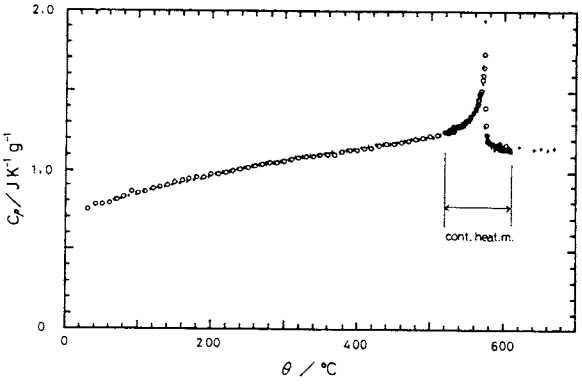

Fig.4 Specific heat capacity of quartz from Brazil. cross: recommended values proposed by Hemingway[1], circle: this work. Specific heat capacity data obtained from the continuous heating measurement (cont. heat. m.) are plotted around transition anomaly after the heat exchange correction explained in Fig.3. The shaded area indicates that the whole data were not drown to avoid too many data-plots from the continuous heating measurement.

70K for the diffuse peak of $Ca_2Co_{0.91}Fe_{0.09}SiO_2$ in Fig.7.

Result and discussion

Heat capacity and transition entropy of åkermanite solid solution

Heat capacit-temperature profiles of synthetic åkermanite solid solutions are shown in Fig.5 to 8 for all data in this work. Fig.5 characterizes great temperature drift from 83℃ to 220℃ with increase of Co content of the Co-åkermanite solid solution. The transition entropies are rather constant as shown in the Table 1. Fe exchange in Co-åkermanite markedly effects peak diffuseness even in a minute exchange below 10 percent as shown in Fig.6. Exchange of Ca with Sr in Co-åkermanite also shows a strong effect on peak diffuseness. At 20 percent exchange with Sr the transition peak vanishes (Fig.7). Zn exchange of åkermanite increases the transition temperature from 83℃ to 130℃ as shown in Fig.8. Despite many trials,

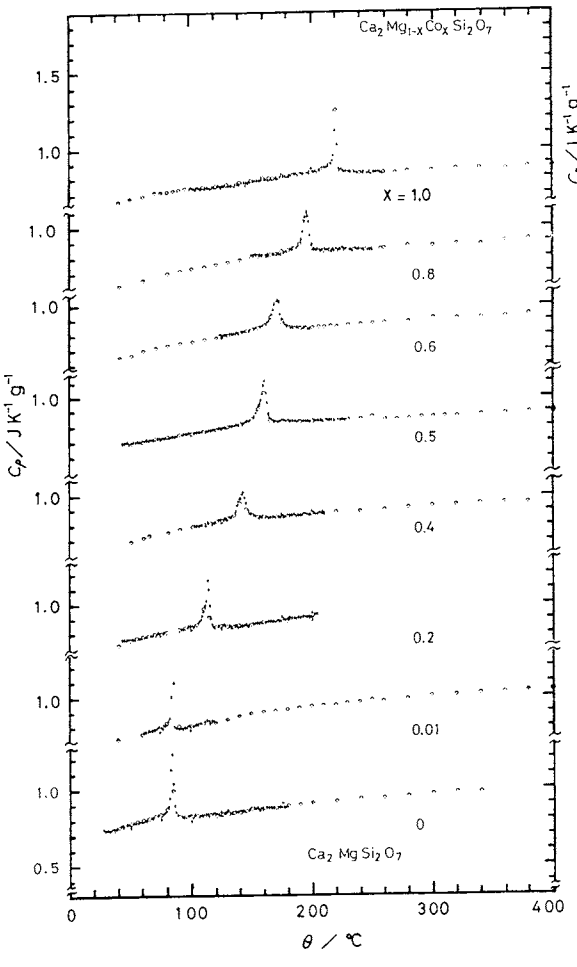

Fig.5 Specific heat capacity vs. θ plot for synthetic Co-exchanged åkermanite. Cross marks in dense plot area were obtained by the continuous heating method. The transition temperatures are strongly influenced with the Co-content.

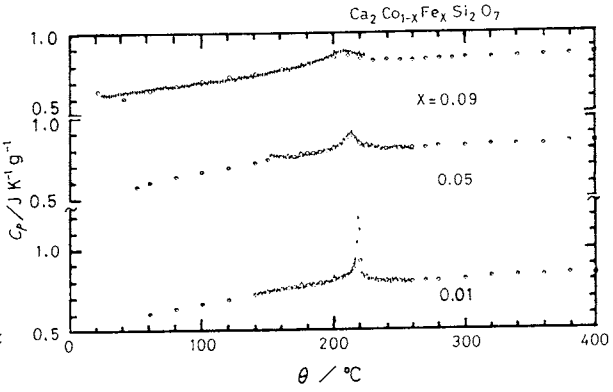

Fig.6 Specific heat capacities of synthetic Fe exchanged Co-åkermanite. Very few amount of Fe exchange results in diffusing of the transition peak.

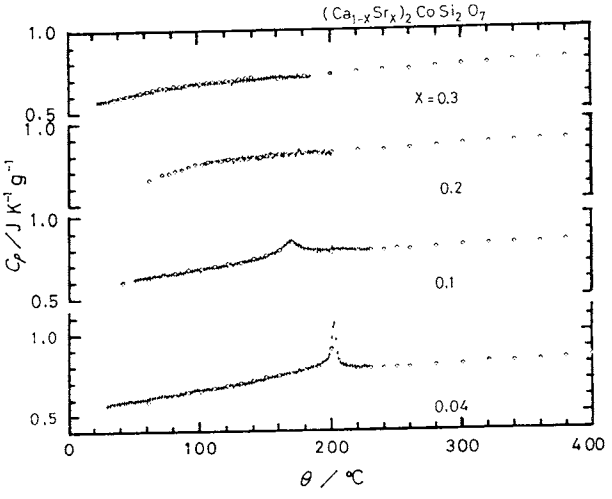

Fig.7 Specific heat capacities of synthetic Ca-Sr exchanged Co-åkermanite. Small amount of Sr makes diffusing of the transition peak. The transition peak disappear in over 20% of Sr-exchange.

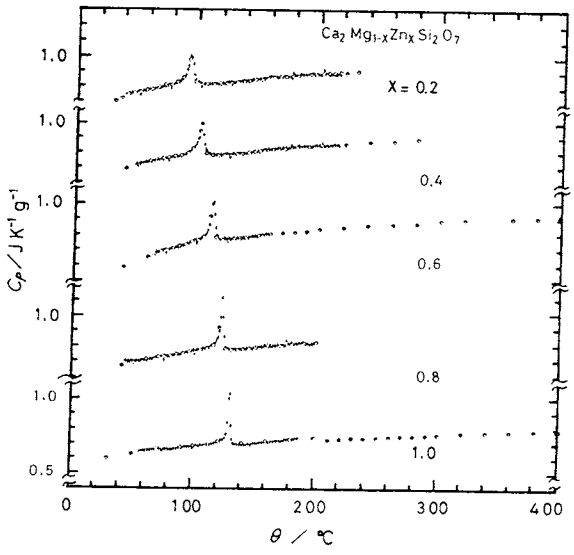

Fig.8 Specific heat capacities of synthetic Mg-Zn exchanged åkermanite.

quantitative explanations of the effects of temperature drift on metal exchange of the solid solution series have so far been unsuccessful[8] and are thus under investigation.

Hysteresis check by cooling run

Although most measurements were performed by the heating run, a cooling measurement was however applied in order to check the hysteresis effect of the transition. A Co-åkermanite sample was heated at a temperature above the transition temperature in the calorimeter, the PID controller was then adjusted to heat leaking or slightly cooling condition, and the t-T relations were measured. If the heat leakage is considered constant in a narrow temperature range, dt/dT-t plot is then analogous to C_p-T plot. The result showed that the transition temperature has no hysteresis. The peak temperature is thus perfectly the same for both heating and cooling runs, which also supports that the transition is of the 2nd-order.

Statistical explanation of the transition entropy

The following evidence should be born in mind for the statistical evaluation of the transition entropy for åkermanite. (1) The transition entropy for all the solid solution series of åkermanite measured is almost constant through the material series (Table 1), 1.7 JK^{-1}mol^{-1}, which suggests the same mechanism for the transition. The small entropy change may be suitable for a statistical evaluation, because there are, in general, few choices of the configurational change on a transition corresponding to the small entropy change. (2) The volume change of the transition was not detected[1] and other contributions, such as magnetic or electrostatic change are negligible. (3) Previous X-ray and electron diffraction works show the presence of about 3 to 4 times incommensurate super lattice for the lower temperature phase. The modulation wave vectors are assigned to be in [110] and [$\bar{1}$10] directions[4]. X-ray refinement of the mean sub-cell structure of the incommensurate phase shows that the direction of Ca-displacement is restricted perpendicular to the mirror plane of the space group $P\bar{4}2_1m$[5].

The last evidence may suggest some local break of the mirror symmetry in the structure. Mean Co-O distances reveal two maximum probability peaks in the incommensurate structure of Co-åkermanite[6]. This fact may show the presence of two sites, compressed and normal, as proposed by Seifert *et al.*[2] for the data obtained from Mössbauer spectra of Fe bearing åkermanite.

The modulation wave-length will be determined as the influence-distance of distortion of a displaced atom at the state of a unit cell in the crystal. In other words, one configuration is likely to exclude the same configuration in neighbouring positions or in a distance (short range order model). We assume for simplicity the distance should be triple the sub-cell periodicity of the Åkermanite case. In addition to this, we select the simplest model in which the only two states, A and B, are allowed in the unit cell, then the number of possible configurations appearing in every three unit cells is eight as follows:

AAA BBB
AAB BBA
ABA BAB
BAA ABB

As there are 2×3=6 formula units($X_2YSi_2O_7$) in the three unit cells, the statistical model gives the amount of entropy for the I-N transition as follows:

$$\Delta S = k \ln 8^{N/(2\times3)} = (R/2)\ln 2 = 2.8815 \mathrm{JK^{-1}mol^{-1}} \quad (3)$$

where k, R and N are the Boltzmann's constant, gas constant and the Avogadro's number, respectively. The statistical model gives a slightly large amount of the transition entropy in comparison with both $1.9JK^{-1}mol^{-1}$ obtained by Hemingway *et al.*[1] and $1.7JK^{-1}mol^{-1}$ of the mean values obtained in the present work. As the eight possible configurations above give lager entropy than the measured values for the transition, the number of configurations should be decreased. The left and right groups of the above configuration array are in a relation of A-B exchange. One possibility will be of large enough domain formation of the individual left and right configurations. The acentric space group, $P\bar{4}2_1m$, of åkermanite may allow such kind of domain formation. Then, the model really gives $\Delta S=k\ ln4^{N/2\times3} = (R/3)ln2 = 1.9210JK^{-1}mol^{-1}$.

The statistical model, that is, the existence of four different configurations for every three unit cells, also suggests reasonable explanation for the periodicity of satellite spots of the electron diffraction. The four configuration is apt to make four times super lattice in average. Therefore we can presume the 3×4 mean super lattice as a modulated structure unit. The tetragonal symmetry generates coexistence of a set of rectangular arrays of the super lattice. This suggests that the modulation wave length should be three or four-times the unit cell dimensions along a given direction. Iishi *et al.* showed the modulation vectors in two dimensions are $k_1=0.2913\times(a^*+b^*)$ and $k_2=0.2913\times(-a^*+b^*)$[4]. The modulation wave length is 3.4328(=1/0.2913) times that of the subcell. Tetragonal symmetry of the diffraction pattern of the modulation structure suggests that the repeating units should be distributed randomly in *a* and *b* crystallographic directions, maintaining the symmetry. Equal abundance of the three and four-times superstructures should give statistical repeating unit in an *a*-direction to be $a' = (3\times4)^{1/2} = 3.4641$, which is very close to the observed value, 3.4328(=1/0.2913).

The above statistical model may not be a unique solution but an accidental coincidence. The interesting point is that almost the same amounts of all the obtained transition entropies independ on the solid solution series, *Cp-θ* profile patterns and temperature ranges of the transition, if they can be measured. Some samples offer so diffuse *Cp-θ* profiles that the entropy value cannot be determined (Fig.7). This may prove the generation of disordering by the atom exchange and eventaully of the high form state at the solid solution without satellites.

Average transition entropy value is 1.727 $JK^{-1}mol^{-1}$ for 17-samples in the Table 1 . If we rewrite eq. (3) as follows;

$$\Delta S = k\ln m^{N/(2n)} = R/(2n)\ \ln\ m\ JK^{-1}mol^{-1} \quad (4)$$

where *n* and *m* represent the unit cell dimensions (as multiple value of the sub-cell dimension) of a mean super lattice for the modulation. (*n*×*m*) means the two dimensional area(/sub-cell area unit) of the unit cell of the super lattice. Table 2 shows a list of entropy values calculated from the eq. (4). The table indicates the possible modulation periodicity corresponding to the statistical model of åkermanite transition.

Hagiya *et al.*[6] showed gradual decrease of satellite intensities for Co-åkermanite with the temperature elevation from room temperature to the transition point, over which the intensities became zero. This may indicate only disordering of modulation periodicity below the transition temperature, whereas the site distinction for individual atoms as a origin of the modulation should remain stable up to the transition temperature. This is because the heat capacity peak at the

Table 2 Entropy values calculated from the eq. (4).

	$\Delta S = [R/(2n)]\ \ln\ m$					
n	1	2	3	4	5	6
m						
2	2.8815	1.4407	0.9605			
3	4.5671	2.2835	1.5223	1.1417		
4	5.7631	2.8815	1.9210	1.4407	1.1526	
5	6.6907	3.3453	2.2302	1.6726	1.3381	1.1151
6			2.4829	1.8621	1.4897	1.2414

Average of underlined values = $1.7445\ JK^{-1}mol^{-1}$ to be considered as reasonable values between 1.5 and $2JK^{-1}mol^{-1}$.
Mean entropy value observed = 1.72 from 17-measurements in Table 1.

transition temperature is sharp enough and no remarkable preliminary effects have been detected in the temperature range (Fig.5), where the satellite intensities decrease.

Numerical data for heat capacities measured in the present work may be furnished on request to the first author (T.M.).

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要　旨

オケルマナイト固溶体は80-250℃の温度領域において，不整合－整合相転移(I-N転移)を行うことで知られている。転移温度は固溶体の組成に依存して変わる。この転移温度付近の熱的挙動を明らかにする目的で，種々の組成のオケルマナイト固溶体結晶を，浮遊帯溶融法によって合成し，少試料断熱型熱量計を用いて，2g以下の試料により，室温以上の温度における熱容量を測定した。求められたI-N相転移エントロピーは平均約1.7$JK^{-1}mol^{-1}$であり，転移温度，組成に関係なくほぼ一定の値であった。転移メカニズムと転移エントロピーの値について変調構造との関係において統計的モデルを論じた。