On the Phase Transition of Hexamethyldisilane

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So-called plastic crystal was first defined by Timmermans[1] in 1938 as a class of crystals which have the entropy of fusion less than about 5 e. u., being miscible together regardless of the difference in the molecular shape, and show much larger plastic flow than the ordinary crystals. This kind of crystal usually undergoes phase transition with much larger entropy change than that at the melting point and the phase just below the melting point possesses a peculiar nature such as that mentioned above. Since then, a number of crystals were found to belong to this category. In general, most of these crystals were composed of more or less globular molecules and these molecules having methyl or methylene groups at the molecular peripheries are the typical case ; i. e., $C(CH_3)_4$[2], $C(SCH_3)_4$[3], cyclohexane[4], $Be_4O(CH_3COO)_6$[5], camphor[6], etc. These kinds of molecules in the lattice are considered to be held together mainly by the weak van der Waals force in respect of the rather small heat of sublimation, and the molecules are characterized by the violent thermal motions such as statistical randomness of molecular orientation or, moreover, by such a factor as self-diffusion which was revealed by recent investigations with nuclear magnetic resonance absorption[7] or in other ways.

In the previous paper[8], the present authors and others have reported the results of preliminary investigations of the phase transition of hexamethyldisilane by thermal and X-ray methods and found that this material really belongs to the category of the plastic crystal. We have also published already the result of the investigation by use of the nuclear magnetic resonance method on the present crystal[9]. So, in the present paper we should like to confine ourselves to reporting mainly the results obtained by the thermal method.

Experimental

Material.—The hexamethyldisilane used in this investigation was prepared by the courtesy of Dr. Nozakura from hexachlorodisilane and the methyl Grignard reagent[10] and purified by

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[8] H. Suga, S. Seki, Y. Chatani and I. Taguchi, *Ann. Report Inst. Fiber Res.* (Osaka Univ.), **8**, 51 (1954), (in Japanese); Y. Chatani, H. Suga and I. Taguchi, Annual Meeting of the Chemical Society of Japan, held at Tokyo, April, 1955.

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[10] W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **61**, 363 (1939).

fractional distillation under ordinary pressure, b.p. 112.8~113.0°C. After repeated fractional crystallizations, the sample obtained was finally purified by vacuum distillation, m. p. 14.2~14.4°C. It has been found in the course of purification that this crystal showed remarkably the so-called "vapor snake" phenomenon[11] which seemed to be characteristic of the crystal having low heat of fusion and high triple-point pressure.

Procedure and Apparatus.—For the reaffirmation of the occurrence of the phase transition, the method of the differential thermal analysis (DTA) was employed by using alumina powder as a reference substance. The sample was distilled into a DTA test tube and then sealed off in vacuo. After cooling down to the liquid nitrogen temperature, the sample was heated at a nearly constant rate 0.75°C/min. The apparatus was similar to that[12] used hitherto in our laboratory except for the automatic controller device for the constant heating rate with the reference substance and also the automatic recording of the temperature difference between the sample and the reference substance. The details of the automatic controller and recorder will be reported elsewhere in the near future. In order to determine the accurate temperatures and enthalpy changes associated with the polymorphic transition and fusion, respectively, the heat capacity was determined over the temperature range from −80 to +40°C with the conduction calorimeter which was the same one[13] used in our laboratory with a slight modification. The sample-containing cell was made anew of eighteen-carat gold plate with a wall thickness of 0.03 cm. and was approximately 2.5 cm. in height and 1.5 cm. in diameter. Eight radial fines of thin platinum sheet were silver-soldered inside the calorimeter to aid in establishing good heat distribution. In order to ensure thermal equilibrium, the heating rate employed was 0.25~0.30°C/min. except for around the transition and fusion points where a much slower heating rate was necessary. The vapor pressure measurements were carried out below and above the melting point of this crystal by using a simple glass-made mercury manometer with a sufficiently degassed sample.

Results and Discussion

Fig. 1. gives the result of the differential thermal analysis. The heat effect accompanied by the phase transition (at about −52°C) was three times as large as that corresponding to the fusion and consistent with the previous preliminary result[8]. The high temperature phase looks uniformly transparent, to a glassy mass, and always accompanies the vapor snake phenomenon as far as the air is absent. The microscopic observation indicates that this phase is optically isotropic. On cooling this phase, it is observed to be converted into a polycrystalline, opaque mass at the transition point where the appearance of the birefringence was observed under the microscopic observation.

The heat capacity data are tabulated in Table I and their variation with temperature is plotted in Fig. 2. Table II gives enthalpy and entropy changes accompanying the transition and fusion processes, respectively. In order to determine the true melting point of hexamethyldisilane and also to test the amout of impurity

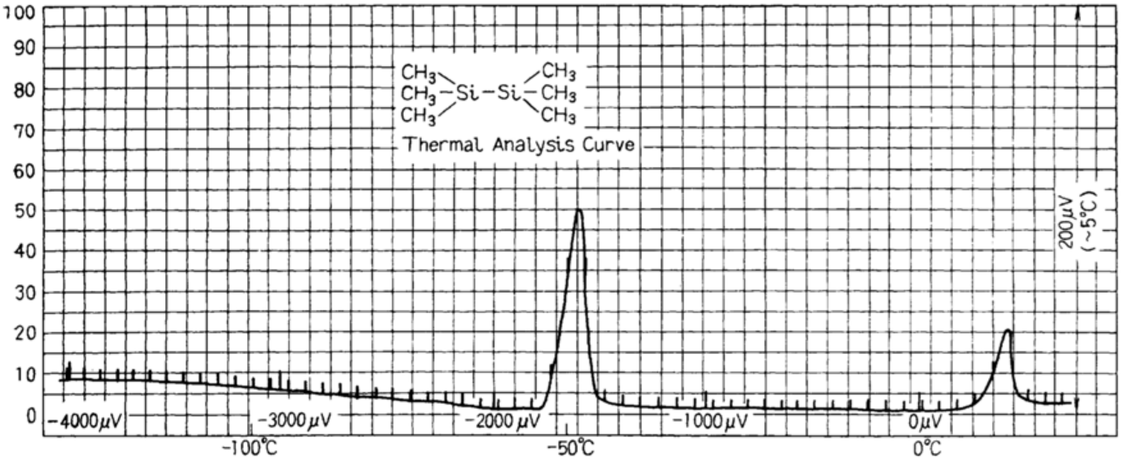

Fig. 1. Automatic recording curve of the differential thermal analysis for hexamethyldisilane.

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[12] H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).

[13] I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**-**9**, 25 (1950); S. Seki, M. Momotani, K. Nakatsu and T. Ōshima, This Bulletin, **28**, 411 (1955).

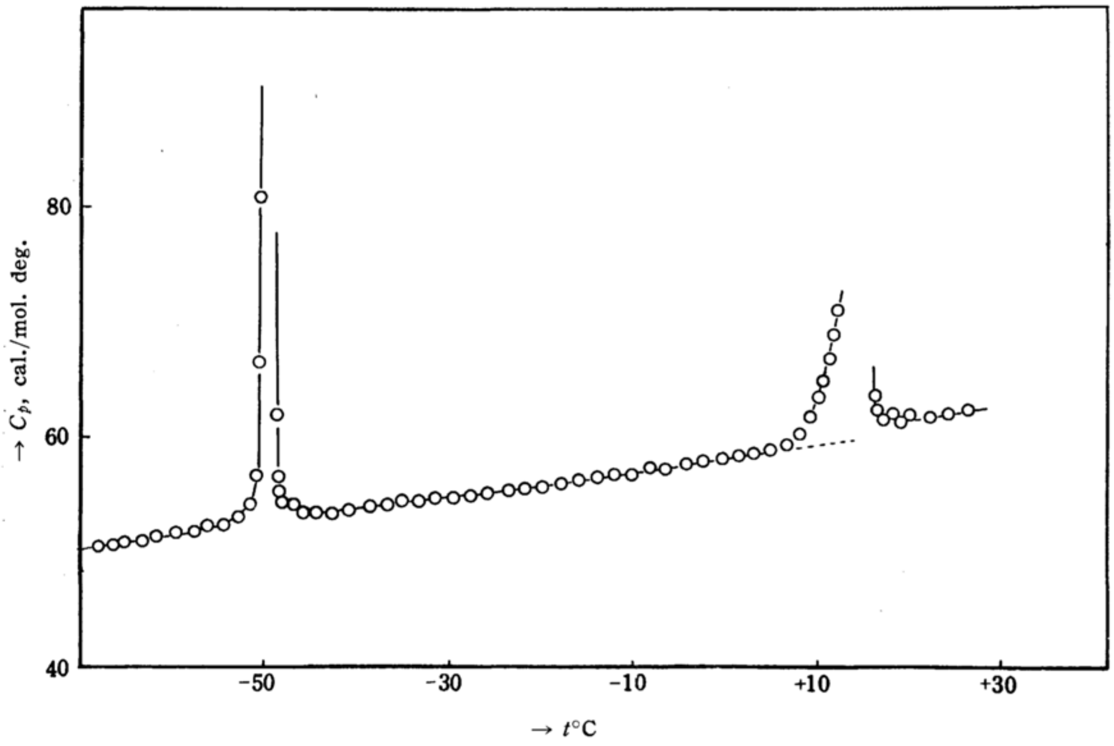

Fig. 2. Heat capacity of hexamethyldisilane as a function of temperature.

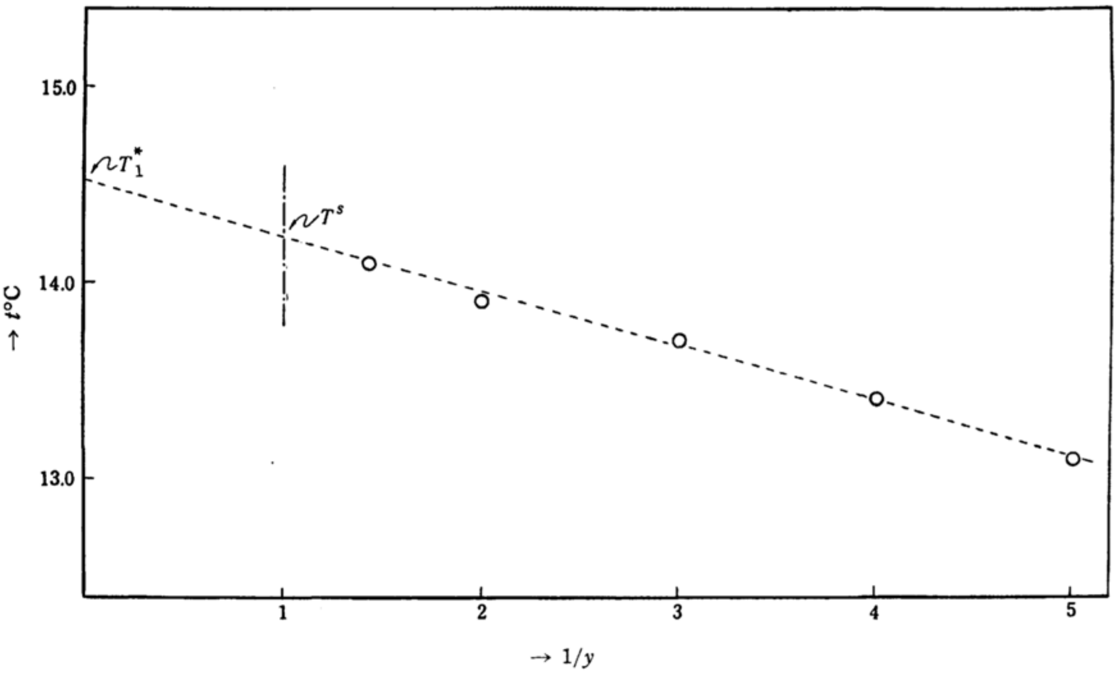

Fig. 3. Plot of the temperature of the liquid-solid equilibrium for hexamethyldisilane as a function of the reciprocal of the fraction of sample melted. T^s is the m.p. of the actual sample, and T_1* is the m. p. of an absolutely pure sample.

TABLE I. C_p OF HEXAMETHYLDISILANE AS A FUNCTION OF TEMPERATURE

t°C	C_p (cal./mol. deg.)	t°C	C_p (cal./mol. deg.)
−66.96	50.76	−21.36	55.10
−63.42	50.46	−18.13	55.08
−61.21	51.40	−12.76	55.45
−57.18	52.21	−10.07	55.58
−55.30	52.27	− 7.59	55.69
−54.39	52.66	− 4.41	56.26
−53.49	53.33	− 1.21	56.64
−52.87	53.77	2.91	58.12
−52.58	62.16	5.28	61.45
— transition —		8.42	66.68
−49.37	74.67	11.39	96.30
−48.13	53.88	12.55	141.32
−47.39	52.96	— fusion —	
−44.70	53.49	16.71	60.19
−41.11	53.61	17.70	61.41
−38.20	53.79	19.22	60.84
−34.39	53.74	21.78	61.44
−30.09	54.27	22.52	61.16
−26.23	54.64		

TABLE II. TEMPERATURES, ENTHALPIES AND ENTROPIES OF TRANSITION AND FUSION OF HEXAMETHYLDISILANE

	T°K	ΔH (cal./mol.)	ΔS(e. u.)
Transition	221.8	2330	10.5
Fusion	287.7_2	721	2.51

TABLE III. VAPOR PRESSURE DATA OF HEXAMETHYLDISILANE IN THE SOLID AND LIQUID STATES

Solid state		Liquid state	
T°K	P, mmHg	T°K	P, mmHg
274.52	7.648	287.62	16.546
275.27	7.917	289.45	18.286
279.14	10.179	291.87	20.850
280.51	11.075	294.34	23.758
282.04	12.190	296.78	26.884
283.61	13.405	299.32	30.664
284.34	14.867	301.54	34.124
286.56	15.831	303.01	36.830
		304.19	38.940
		307.09	44.853
		310.39	52.037

$\log P=-2105.37/T+8.550$ (in the solid state)
$\log P=-1953.12/T+8.011$ (in the liquid state)

	ΔH(cal./mol.)	ΔS (e. u.)	$\Delta G^0_{298.16}$
Sublimation	9640±25	25.96±0.17	1900±76
Vaporization	8943±16	23.49±0.05	1940±32
Fusion	697±41 (obsd. 721)		

TABLE IV. ENTROPIES OF TRANSITION AND FUSION OF HEXAMETHYLDISILANE AND ALSO OF RELATED COMPOUNDS AVAILABLE FOR COMPARISON

	$Si_2(CH_3)_6$ a)	Si_2F_6 b)	$C_2(CH_3)_6$ c)	C_2F_6 d)	C_2Cl_6 e)
ΔS_{tr}	10.5	—	3.13	8.59	1.93 5.70
ΔS_f	2.51	13.8	4.82	3.71	5.50
ΔS_{total}	13.0	13.8	8.0	12.3	13.1

a) Present study.

b) The values were quoted from F. D. Rossini et al., "Selected values of Chemical Thermodynamic Properties", U.S. Government Printing Office, Washington (1952).

c) D. W. Scott and H. M. Huffman, *J. Am. Chem. Soc.*, **74**, 883 (1952). Recent dilatometric observation revealed another instance of polymorphism near the m. p. [W. F. Seyer, R. B. Sennet and F. C. Williams, *J. Am. Chem. Soc.*, **71**, 3447 (1949)].

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involved in the used sample, the well-known thermodynamic equation[14]

$$T=T_1^*-(\boldsymbol{R}T_1^{*2}/\Delta H_f)(N/y)$$

was used. Here, T and T_1^* are the apparent and true melting points of the material, respectively; $\boldsymbol{R}$, gas constant; ΔH_f, the enthalpy of fusion; N, the number of moles of impurity; and y, the number of moles of material melted. Fig. 3 represents a plot of equilibrium temperatures against the various amounts melted. As is shown, the observed T versus $1/y$ relationship gives a straight line whose slope makes it possible to determine the value of N, by using the measured value of ΔH_f. As the result, we have determined the true melting point of hexamethyldisilane to be 14.5_6°C and the purity of the sample was 99.87% pure (the m. p. reported in the literature is 14.0∼14.4°C[15]).

Table III gives the vapor pressure data of the liquid and solid states. The observed values in the liquid range are in good agreement with those of Brockway and Davidson[15]. By applying the method of least squares, good linear relations are obtained between $\log P$ and $1/T$ in both phases. The table also includes the changes of free energy, enthalpy and entropy accompanying the vaporization and sublimation processes, respectively. As the difference between the heat of vaporization and of sublimation, one can obtain the heat of fusion 697±41 cal./mol. which agrees within their experimental errors with the calorimetric value mentioned above.

We summarize in Table IV the entropies

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[14] For example, S. Seki, *Japan Analyst* (*Bunseki Kagaku*), **6**, 737 (1957).

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of the transition and of the fusion of the present substance together with those of the related compounds. As is evident for all compounds except for C_2Me_6, the sum of both entropies of the transition and fusion is nearly equal to 13.0 e. u., the value predicted from the Walden rule[16], which holds for the entropy of fusion of usual organic compounds. Accordingly, the transition phenomenon of these compounds may be reckoned as the beginning of the melting process. In other words, the total amount of entropy change which ordinarily should be gained at the melting point is divided between the transition and the melting processes. In the case of hexamethyldisilane, the observed entropy of fusion is very close to the value 2.0 e. u. calculated theoretically for a communal entropy of fusion[17], which comes from the communal sharing of free volume in the liquid state. Considering the reverse (freezing) process, it may be reasonable to infer that the liquid of hexamethyldisilane freezes only with respect to the translational motion** of the molecule at the freezing point and does not do so with respect to the rotational or orientational motion until the transition point is reached. And, even at the transition point, it seems that the stopping of the rotational motion of the methyl group about the Si–C axis does not take place yet. This is because the sum of the entropies of fusion and of transition for hexamethyldisilane is almost equal to that for hexachlorodisilane which is isoelectronic with the former and possesses no corresponding rotational group. This thermodynamical conclusion coincides with the result obtained from the nuclear magnetic resonance experiment[9] which revealed that the rotational motion of the methyl group about the Si–C axis was already excited even at temperatures far below the transition point.

In the X-ray investigation[8] of hexamethyldisilane, it was found that the high temperature phase belongs to body-centered cubic lattice with the cell constant of 8.47Å (at 0°C) containing two molecular units and that the molecular axis (Si–Si axis) is orientated randomly among the four body-diagonals. The observed reflection lines were also interpreted semiquantitatively by assuming a D'_{3h} model (internal free rotation about the Si–Si axis), or alternatively assuming either a D_{3d} or a D_{3h} model combined with overall rotation of the molecule about the molecular axis, by using the value 18 for the temperature factor in all cases. On the other hand, the crystal structure of the low temperature phase was not yet determined, owing to the difficulty of preparing a single crystal available for the X-ray analysis (it may be hexagonal or orthorhombic crystal system[8]). The anomalously large value of the temperature factor in the high temperature phase is qualitatively in accordance with the large value of the entropy of transition. In passing it may be added here that the studies of Raman and infrared spectra[18] of hexamethyldisilane revealed that the molecule in the liquid state has a D_{3h} or a D'_{3h} equilibrium configuration, excluding a D_{3d}-type.

Now, we shall infer from the entropy consideration what sorts of molecular motions will be excited on passing through the transition point from the ordered low-temperature phase to the plastic crystal phase. Referring to the results of X-ray and spectroscopic investigations mentioned above, the following model may be assumed reasonably. In the high temperature phase, the molecular orientation (motion 1) is randomly distributed among the four body-diagonals and the two kinds of internal rotation (motion 2, about Si–Si axis; motion 3, about Si–C axis) combined with the overall molecular rotation about the molecular axis (motion 4) are fully excited, whereas the motions are highly hindered except for motion 3 in the low temperature phase though not so below the transition point[9]. Then each contribution from the enhancement of such a kind of motion to the entropy of transition can be estimated in terms of statistical mechanics. The contribution from the increase of the orientational freedom (motion 1) is $\boldsymbol{R} \ln 4$ which amounts to 2.54 e. u. The contribution from motion 2 is calculable by use of Pitzer's table[19], assuming the symmetry number 3 and the potential barrier hindering the internal rotation in the low temperature phase 5.7 kcal./mol.[9] In this case, the moment of inertia is computed

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** It may be noted that even in the plastic crystal phase a kind of self-diffusion process seems to occur (see Ref. 9).

[16] P. Walden, *Z. Elektrochem.*, **14**, 763 (1908).

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[19] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937); K. S. Pitzer and W. D. Gwinn, ibid., **10**, 428 (1942).

using tetrahedral angle for ∠Si–Si–C and the interatomic distance of Si–C, 1.88 Å[20], and also assuming that the three rotating hydrogen atoms in methyl group lie at the position of the carbon atom. This contribution amounts approximately to 2.58 e. u. The sum of both entropies, 5.1 e. u., is only half of the observed entropy of transition, 10.5 e. u., so the remaining contribution from motion 4 seems to amount to nearly equal magnitude. Although the precise estimation of the latter is difficult at the present stage owing to the lack of knowledge about the crystal structure of the low temperature phase and also about the heights of the potential barrier hindering this motion in both phases, we assume tentatively that the rotation is fully excited in the high temperature phase whereas the motion is entirely fixed in the low temperature phase. Then the contribution can be calculated with the following equation

$$\varDelta S = \boldsymbol{R}\left[\ln\frac{1}{\pi\sigma}\left\{\frac{8\pi^3 I_m \boldsymbol{k} T}{\boldsymbol{h}^2}\right\}^{1/2}+\frac{1}{2}\right]$$

where I_m is the moment of inertia about the molecular axis, and σ the symmetry number. The calculated value becomes 5.50 e. u. with the values of $T=222$°K and $\sigma=3$. Thus, the calculated total amount of these three entropies, 10.6 e. u., comes out to be nearly equal to the observed one, 10.5 e.u. Here it may be noticed that we have not completely ignored the overall rotational motions about the other two principal axes, since these motions were partly involved already in motion 1. Probably this fortuitous agreement arises from the situation that the over-estimated entropy value of motion 4 might be canceled by the under-estimaton of motion 1.

In conclusion, we may say that although our discussion on the mechanism of the phase transition in hexamethyldisilane from the point of view of entropy is of semi-quantitative nature, its main feature was explained by combining our thermodynamical study with those of the X-ray crystal analysis and the nuclear magnetic resonance.

Summary

Measurements of the heat capacity (200～300°K) and the vapor pressure (274～310°K) were carried out covering the transition and melting points of hexamethyldisilane. The following results were obtained; T_{tr} 221.8°K, $\varDelta H$(transition) 2330 cal./mol., $\varDelta S$(transition) 10.5 e. u.; T_f 287.7$_2$°K, $\varDelta H$(fusion) 721 cal./mol., $\varDelta S$(fusion) 2.51 e. u.; vapor pressure equations,

$$\log P(\mathrm{mmHg}) = -2105.4/T + 8.5503 \quad (274.5\sim286.6^\circ\mathrm{K})$$

$$\log P(\mathrm{mmHg}) = -1953.1/T + 8.0105 \quad (287.6\sim310.4^\circ\mathrm{K});$$

$\varDelta H_{sub}$ 9640±25 cal./mol., $\varDelta S_{sub}$ 26.0±0.17 e.u., $\varDelta G^\circ_{298.16}$(sub.) 1900±76 cal./mol.; $\varDelta H_{vap}$ 8943±16 cal./mol., $\varDelta S_{vap}$ 23.5±0.05 e. u., $\varDelta G^\circ_{298.16}$(vap.) 1940±31 cal./mol.

These data showed that the present crystal belongs to the class of plastic crystal. We have discussed the qualitative nature of the phase transition in the present crystal from the point of view of entropy, referring to the X-ray and the nuclear magnetic resonance studies. The remarkable "vapor snake" phenomenon was also observed on this material.

In conclusion, the authors wish to express their sincere thanks to Professor I. Nitta for his valuable advice and continued interest in the present study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education to which the authors' thanks are due.

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