Deuteron Magnetic Resonance Studies of Structures and Phase Transitions in the Tantalum-Deuterium System

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The deuteron magnetic resonance in the tantalum-deuterium system has been measured as a function of the composition (0.45 to 0.198 D/Ta) and of the temperature (90 to −179°C), and the results has been discussed in relation to the neutron diffraction and the heat capacity data. The most probable arrangement of the deuteriums in the polymorphic varieties has been proposed. For the low temperature form (β_1 form), it has an ordered structure which belongs to the space group $A222$, with the four tantalums at the $4K$ positions and the two deuteriums at the $2a$ positions. Since the deuterium positions are described by a single Z' principal axis direction, which coincides with the c axis, the quadrupole coupling constant is not averaged by the rapid diffusion of the deuteriums. For the intermediate temperature form (β_2 form), a structure constructed with four types of domains has been proposed. In this structure, the space group is the same as that of the β_1 form, and the deuterium positions in the domains are $2a$, $2b$, $2c$, and $2d$ respectively. For the high temperature form (α form), the observed quadrupole coupling constant, which is averaged to zero, can be accounted for if the deuteriums are randomly distributed over all the available tetrahedral sites. However, the calculated configurational entropy based on this assumption is larger than the measured value.

It is a well known phenomenon that many transition metals absorb hydrogen under appropriate conditions.[1] As for the tantalum, the solubility extends to about 44 atomic percent at 200°C and under a 1 atomosphere. However, when the temperature decreases below 60°C, a new phase (β phase) based on the composition Ta_2H is formed.[2,3]

According to the X-ray diffraction study,[2] the high temperature phase (α phase) possesses a body centered cubic structure of elementary tantalum, while the low temperature phase (β phase) is a body centered tetragonal with an axial ratio of $c/a=1.008$. Saba, Wallace, Sandmo, and Craig have measured the heat capacity of Ta_2H[4] from 12 to 555°K and have found three λ points, indicating that the following four forms exist; β_1 below 306°K, β_2 between 306 to 332.5°K, β_3 from 332.5 to 333.5°K, and α above 333.5°K. They have also estimated the configurational entropies. They were zero, 0.7, 3.3, and 4.9 e.u.mol^{-1} for β_1, β_2, β_3, and α respectively. Since there are 12 tetrahedral sites available for each hydrogen atom, they attributed the λ points to the rearrangement of hydrogen among these sites.

The neutron diffraction study by Wallace[5] has shown that the β_1 form is pseudocubic, with $a=2a_0=6.74$ Å, where a_0 is a lattice constant for the β_2 form. He proposed three configurations which satisfied the neutron diffraction intensities for the β_1 form. One of the structures, which he denoted structure A, belongs to the space group $I4$, with half deuteriums located at the general positions of 1/4 1/8 0 and 5/8 0 1/4. To account for the contradiction between the proposed structure and the vanishing residual entropy for the β_1 form, he proposed a structure with a high local order in domains which are not large enough to give rise to superstructure diffractions.

To solve the above contradiction, this problem in the ordered structure of Ta_2D has been discussed in a series of paper.[6-8] Among the three proposed structures, however, the superlattice diffraction reliability factors of the first two structures[6,7] are appreciably worse than that of Wallace's disordered structure. The best agreement with the experimental results was obtained by Petrunin, Somenkov, Shil'shtein, and Chertkov (hereafter abbreviated as PSSC), who took into account the displacement of the Ta atom. This structure is orthorhombic and belongs to the space group $A222$, with $a\approx b\approx\sqrt{2}\,a_0$ and $c\approx a_0$. The four Ta atoms are located at the 4K positions ($-x$ 0 0, 1/2+x 1/2 0, $-x$ 1/2 1/2, 1/2+x 0 1/2), and the two deuterium atoms at the $2a$ positions (1/4 1/4 1/4, 1/4 3/4 3/4). The displacement parameter, x, which was so determined as to minimize the reliability factor, was 0.012, while the minimized reliability factor, for the superlattice diffraction was 0.107.

Among the four proposed structures cited above, the reliability factor for the PSSC ordered model with the displacement of Ta is the smallest, and that for Wallace's model is next. However, one may obtain additional information from the deuteron magnetic resonance. The main purpose of this paper is to obtain additional information on the arrangement of deuteriums in the polymorphic varieties of Ta_2D through studying the deuteron magnetic resonance, which is very sensitive to the position and the translational motion of the deuteriums.

Experimental

Deuterides of tantalum with compositions ranging from

1) G. G. Libowitz, *J. Nucl. Mater.*, **2**, 1 (1960).
2) T. R. Waite, W. E. Wallace, and R. S. Craig, *J. Chem. Phys.*, **24**, 634 (1956).
3) P. Kofstad, W. E. Wallace, and R. S. Craig, *J. Amer. Chem. Soc.*, **81**, 5015 (1959).
4) W. G. Saba, W. E. Wallace, H. Sandmo, and R. S. Craig, *J. Chem. Phys.*, **35**, 2148 (1961).
5) W. E. Wallace, *ibid.*, **35**, 2156 (1961); **41**, 3261 (1964).
6) G. Palenik, *ibid.*, **41**, 3260 (1964).
7) V. A. Somenkov, A. V. Gurskaya, M. C. Zemlyanov, M. E. Kost, N. A. Chernoplekov, and A. A. Chertkov, *Soviet Phys. Solid State*, **10**, 2123 (1969).
8) V. A. Petrunin, V. A. Somenkov, S. Shil'shtein, and A. Chertkov, *Soviet Phys.-Crystallogr.* **15**, 137 (1970).

0.45 to 0.198 D/Ta were prepared by a direct reaction of a known amount of deuterium gas with a known amount of Ta metal powder.

The deuteron magnetic resonance measurements were made using a Varian VF-16 wide line spectrometer operating at 6.53 MHz. The temperatures of the samples from −180 to +90°C were obtained with a Varian variable-temperature accessory.

Results

Deuteron Resonance at Room Temperature. At room temperature, the deuteron resonance of the powdered TaD_n (n=0.45, 0.43, 0.375) consists of two parts; one is at the center of the Larmor frequency, and the other consists of a pair of lines located symmetrically around the Larmor frequency (Fig. 1). The intensity ratio of the central line relative to the two satellite lines increased with a decrease in the deuterium concentration. Since the line width of the satellite lines was broad and the intensity was weak, the satellite lines could not be observed for the samples with deuterium concentrations lower than 0.33/Ta. The integrated intensities of the two components are shown in Fig. 2. The extrapolated intensity of the satellite lines to the lower D/Ta value becomes zero at a D/Ta value between 0.2 to 0.15. If we take into consideration the experimental facts that the solubility of hydrogen in Ta metal is about 20%, and that above this concentration the β Ta_2H phase develops,[2,3] the central line can be assigned to the deuteron resonance of the α Ta, and the satellite lines, to that of the β Ta_2D. The theoretical powder pattern line shape in the presence of quadrupole interaction due to nuclei with I=1 has been calculated.[9,10] We have thus smoothed the theoretical line shape with the Gaussian distribution of various values of the root mean square line width (σ). The results are shown in Fig. 1-(A); a more detailed analysis of the powder pattern for an asymmetric field gradient is shown in the Appendix. From the method described in the Appendix, the quadrupole coupling constant, e^2qQ/h, 33.9 KHz, and the asymmetry parameter, η, 0.15 to 0.25, were obtained.

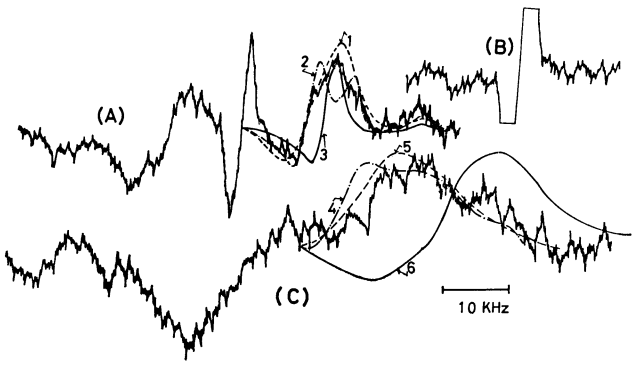

Fig. 1. Observed deuteron resonance signals (derivatives) of $TaD_{0.43}$. (A) R.T. (B) +62°C (C) −179°C. Smoothed curves (1—6) are drawn with various values of asymmetry parameter and σ.

	e^2qQ/h	$\sigma/(3\ e^2q\ Q/4h)$	η
1	33.9 KHz	0.10	0.15
2	33.9 KHz	0.05	0.23
3	33.9 KHz	0.05	0.03
4	33.9 KHz	0.15	0.45
5	33.9 KHz	0.25	0.30
6	67.8 KHz	0.10	0.03

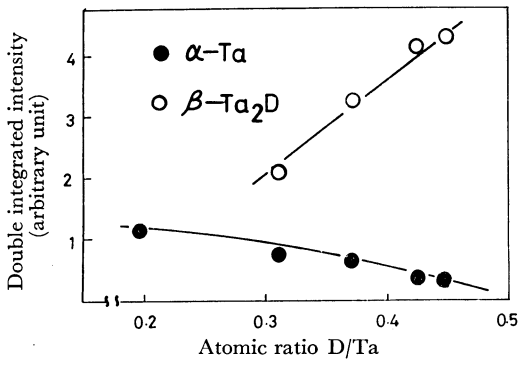

Fig. 2. Concentration dependence of double integrated signal intensity of deuteriums in α Ta and β Ta_2D.

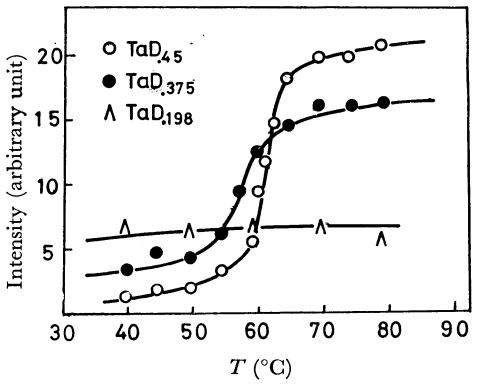

Fig. 3. Temperature dependence of signal intensity of deuteriums in α Ta.

Deuteron Resonance and Phase Transition above Room Temperature. When the TaD_n (n=0.45, 0.43, 0.375) was warmed from room temperature, the deuteron resonance signal intensity of the α Ta began to increase, and that of the β form began to decrease. The signal intensity of the former continued to increase even after that of the β Ta_2D was vanishingly small, but finally it became constant. As shown in Fig. 3, the temperature range where the phase transition proceeded was about 10°C for the $TaD_{0.45}$ sample. The phase transition temperature, which we define as the middle point of the temperature-signal intensity curve, depended on the composition of the sample. As the deuterium concentration decreased, the temperature range of the phase transition became broad and the phase transition temperature became obscure. For the $TaD_{0.198}$ sample, the signal intensity of the α form did not change over the temperature range from +90 to −50°C. For this composition, therefore, most of the deuteriums dissolve in the α Ta metal.

Deuteron Resonance below Room Temperature. As the temperature of the samples decreased, the deuteron signal intensity of the α Ta decreased until it vanished in the temperature range from −30 to −70°C. The

9) M. H. Cohen and F. Reif, "Solid State Physics," Academic Press, New York (1957), Vol. 5, pp. 338—343.
10) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1959).

temperature at which the signal vanished depended on the sample composition; *i.e.*, it was about $-30°C$ for $n=0.45$ and about $-70°C$ for $n=0.198$. As the temperature decreased, the line width of the β Ta_2D became broad. However, even at $-180°C$, the line shape corresponds to that which has nearly the same quadrupole coupling constant smoothed with a broad Gaussian distribution (Fig. 1-(C)).

Discussion

Deuterium Arrangement in β_1 Ta_2D. To account for the experimental results, it is necessary to calculate the electric field gradient (EFG) at the interstitial deuterium atoms. No precise calculation of EFG at interstitial atoms has yet been made. Bloembergen and Rowland[11] have used a Thomas-Fermi approximation by Mott and Jones[12] and have calculated the EFG at monovalent solvent Cu atoms in Cu–Zn substitutional alloy, where the EFG is produced by the extra positive charge of the divalent solute Zn. A similar treatment has been made by Schreiber and Cott[13] for the calculation of EFG at La in the La–H interstitial system. Coogan and Gutowsky[14] applied this approximation in their calculation of the potential energy for hydrogen diffusion in the Ti–H system. Our problem in the EFG calculation is similar to that of the last case. However, in order to know the arrangement of deuteriums, it is not necessary to know the exact solution of the EFG calculation. What it is desirable to know is the relative sign, the relative magnitude, the principal axis direction, and the asymmetry parameter of the EFG tensor. These parameters, fortunately, are determined only by the array of Ta and deuterium ions and are almost independent of the method of estimation of the conduction electron contribution.[15] In this section, we used Mott's screened potential. By using this, we do not expect to have a completely exact solution of the principal value of the EFG tensor, but can obtain the relative magnitude, the relative sign, the principal axis direction, and the asymmetry parameter of the EFG tensor.

Here we choose a set of orthogonal axes, X', Y', and Z' as the principal axes; the Z' axis lies along the direction of the maximum component, and X' along that of the minimum component. The maximum component, eq, at the i-th deuterium atom may be expressed as;

$$eq = \frac{\partial^2 V}{\partial Z'^2} = \sum_j V''(r_{ij}) \frac{(3\cos^2\theta_{ij}-1)}{2} \qquad (1)$$

where $V''(r_{ij})$ is the field gradient along the ij direction and is given by;

$$V''(r_{ij}) = \frac{2Z_j e}{r_{ij}^3}(1+Kr_{ij}+(Kr_{ij}/2)^2)\exp(-Kr_{ij}) \qquad (2)$$

where r_{ij} is the distance between the i-th deuterium and the surrounding j-th ion, θ_{ij} is the angle between the Z' axis and the ij direction, $Z_j e$ is the charge on the j-th ion, and the summation is made over the j-th ions. When the crystal is cubic the EFG at each site is axially symmetric. However, since the low temperature form (β form) is a slightly distorted cubic form, with $c/a=1+\Delta$, where Δ is a small quantity compared with 1, the EFG is not axially symmetric.

Next, we will calculate the EFG for the deuterium arrangement proposed by Wallace.[5] Structure A, which he assumed to be most reasonable,[16] belongs to the $I4$ space group ($a=2a_0=6.74$ Å) with half deuteriums located at the general positions of 1/4 1/8 0 and 5/8 0 1/4. We denote the 8 positions at 1/4 1/8 0, 7/8 1/4 0, 3/4 7/8 0, 1/8 3/4 0, 5/8 0 1/4, 3/8 0 1/4, 0 3/8 1/4, and 0 5/8 1/4 as TA1, TA2, ·····, TA8, the other 8 positions are, of course, at $+1/2$ $1/2$ $1/2$ translation. Due to r_{ij}^{-3} and $\exp(-Kr_{ij})$ terms in Eq. (2), the EFG due to ions other than the nearest neighbor Ta ions can be disregarded. Then, eq and the asymmetry parameter are;

$$eq = -\frac{2}{5}V''(R_1) - \frac{2}{5}V''(R_2) - \frac{12}{25}\Delta V''(R_2) \qquad (3)$$

$$\eta = 3(1-V''(R_2)/V''(R_1)) - \frac{6}{5}\Delta < 3(1-(R_1/R_2)^3) - \frac{6}{5}\Delta \qquad (4)$$

where $R_1=\sqrt{5}\,a_0/4$ and $R_2=\sqrt{5}\,a_0\,(1+4\Delta/5)/4$ are the deuterium–tantalum distances, and the principal axis directions are;

$Z'\|a$, $Y'\|b$ and $X'\|c$ axes for TA2, TA4, TA5, and TA6

$Z'\|b$, $Y'\|a$ and $X'\|c$ axes for TA1, TA3, TA7, and TA8

From the above considerations, one may draw the following conclusion. When the temperature increases and the jump frequency becomes larger than the quadrupole coupling constant of the deuterium atom, each deuterium atom will experience two sites with different principal axis directions and the quadrupole coupling constant will be averaged. Consequently, the following predictions will be realized; (1) the largest principal component will be $eq(1-\eta)/2 \approx eq/2$; (2) the direction of the largest principal component will become parallel to the c axis, and (3) the asymmetry parameter will become zero. Therefore, the quadrupole coupling constant at a low temperature must be twice that at a high temperature as long as the above situation holds.

The ordered deuterium arrangement proposed by PSSC is shown in Fig. 4. It can easily be seen from the $2a$ positions of the deuteriums and the pseudo-tetragonality of the cell that, in the absence of a displacement of the Ta atoms, the EFG at the deuteriums in this ordered arrangement is axially symmetric with respect to the c axis. However, if we consider the fact that the displacement of Ta atoms at $\pm x$ improves the neutron diffraction reliability factor, the EFG is thought to be distorted from the axial symmetry. The maximum principal component, eq, and the asymmetry parameter, η, calculated from the nearest neighbor

11) N. Bloembergen and J. J. Rowland, *Acta Met.*, **1**, 731 (1953).
12) N. F. Mott and G. H. Jones, "Theory of the Properties of Metals and Alloys," Oxford Univ. Press, New York (1936), p. 86.
13) D. S. Schreiber and R. M. Cott, *Phys. Rev.*, **131**, 1118 (1963).
14) C. K. Coogan and H. S. Gutowsky, *J. Chem. Phys.*, **36**, 110 (1962).
15) M. Pomerantz and T. P. Das, *Phys. Rev.*, **119**, 70 (1960).
16) The other two structures which Wallace denoted as Structure B and C give the same result as Structure A.

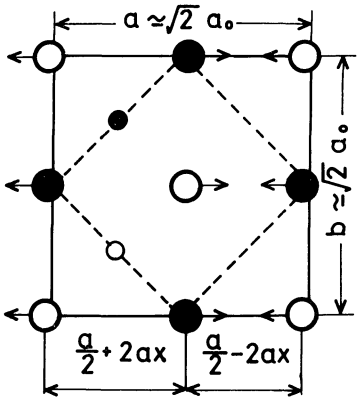

Fig. 4. Projections onto 001 plane of β_1 Ta_2D (PSSC model) Ta's are at $z=0$ (large opened circles) and at $z=1/2$ (large closed circles). D's are at $z=1/4$ (small opened circles) and $z=3/4$ (small closed circles).

four Ta atoms are;

$$eq \approx \left(-\frac{4}{5}+\frac{48}{25}+\frac{96}{25}x\right)V''(R_3) \quad (5)$$

$$\eta \approx 24x \quad (6)$$

where $R_3=\sqrt{5}\,a_0(1+(8x+\Delta)/5)/4$. Since the deuteriums in this ordered structure are situated in a special position, whose Z' direction is parallel to the c axis, the quadrupole coupling constant is not averaged by the rapid diffusion of the deuteriums; that is, the quadrupole coupling constant at a low temperature must be the same as that at a high temperature. Therefore, in order to determine which of the proposed structures is consistent with the deuteron magnetic resonance results, it is sufficient to know; (1) whether the asymmetry parameter at a high temperature is zero or larger than zero ($\approx 24x$), or (2) whether the quadrupole coupling constant at a low temperature, where the deuterium diffusion is negligible, is twice that at a high temperature.

In the previous section, we have shown that the asymmetry parameter at room temperature lies between 0.15 to 0.25, appreciably larger than zero. In order to examine (2), it is necessary to know the correlation time for deuterium diffusion at −179°C. We obtained the correlation times for hydrogen diffusion at −180°C by an extrapolation method by using the proton magnetic resonance data of the TaH_n interstitial system.[17] These times are 10^{-4} and 1.4×10^{-4} sec for $n=0.66$ and 0.1 respectively. The correlation time for deuterium diffusion is expected to be longer than that for hydrogen diffusion due to the isotope effect. Therefore, we assume that $1/\tau_c \ll e^2qQ/\hbar$. As is shown in Fig. 1, the observed spectrum at −179°C can not be expressed as having twice as large quadrupole coupling constant as that at room temperature. It is better expressed as having approximately the same quadrupole coupling constant as that at room temperature, and it is smoothed with a broad Gaussian distribution. From these considerations, it seems that the ordered arrangement proposed by PSSC is the most probable structure for the β_1 form. The calculated eq, asymmetry parameters and configurational entropies for the other two structures,[6,7] together with the above two, are listed in Table 1.

Deuterium Arrangement in β_2 Ta_2D. According to the neutron diffraction study by Wallace,[5] the unit cell of this form ($a=a_0=3.37$ Å) is the same as the X-ray unit cell, which contains one deuterium and two tantalums. There are 12 tetrahedral sites in a unit cell. According to Wallace's notation, these are T_1, T_2, ···, T_6 at 1/2 1/4 0, 1/2 3/4 0, 1/4 1/2 0, 3/4 1/2 0, 0 1/2 1/4 , and 1/2 0 1/4, while the other 6 sites are T'_1, T'_2, ···, T'_6 at a +1/2 1/2 1/2 translation. If the crystal is cubic, these 12 sites are structually equivalent. However, since the β_2 is a slightly distorted cubic form, these 12 sites may be divided into S and L groups,[5] S group contains T_5, T_6, T'_5, and T'_6, while L contains the other 8 sites. There are only three arrangements, random distribution in the S sites, in the L sites, and in all the sites. The calculated neutron diffraction intensities for these three arrangements showed an excellent agreement with the experimental results.[5]

The EFG of these 12 sites may be calculated by means of Eqs. (3) and (4) and by substituting $x=0$ in Eqs. (5) and (6). The resulting Z' direction are shown in Table 2. By using consideration similar to that used previously, one may easily reach the following conclusions;

(1) If the deuteriums are distributed over all the tetrahedral sites with equal probability and with a rapid translational motion, the resultant quadrupole coupling constant will be averaged and will become zero (for b. c. c.) or below the level of detection (for b. c. t.)

Table 1. Calculated eq, η and configurational entropies(S_c) for the various proposed β_1 Ta_2D structures

	Space group	Deuterium positions	R[a]	$(eq)_H/(eq)_L$[b]	η[c]	S_c (e.u. mol^{-1})
Wallace[5]	$I4$	$8G$(1/4 1/8 0) $8G$(5/8 0 1/4)	0.17	1/2	c)	2.7
Palenik[6]	$I\bar{4}$	$8G$(0 1/4 1/8)	0.29	1	0	0
Somenkov *et al.*[7]	$Pnnn$	a(1/4 1/4 1/4) b(1/4 3/4 3/4)	0.30	1	0	0
Petrunin *et al.*[8]	$A222$	$2a$ (1/4 1/4 1/4)	0.107	1	$\approx 24x$[d]	0

a) Superlattice diffraction reliability factor.
b) Ratio of eq at a high temperature to that at a low temperature.
c) At a high temperature; $\eta=0$ and, at a low temperature; η is given by Eq. (4).
d) $x=0.012$ at a room temperature, $x=0.017$ at a liquid nitrogen temperature.

17) B. Pederson, T. Krogdahl, and O. E. Stokkeland, *J. Chem. Phys.*, **42**, 72 (1965).

TABLE 2. CALCULATED Z′ AXIS DIRECTION FOR EACH OF THE 12 TETRAHEDRAL SITES OF THE β_2 FORM

Group		Z' axis direction
L	T_1, T_2, T_1', T_2'	$Z'\|\|$ b axis
	T_3, T_4, T_3', T_4'	$Z'\|\|$ a axis
S	T_5, T_6, T_5', T_6'	$Z'\|\|$ c axis

(2) If the deuteriums are distributed over the L sites, the resultant quadrupole coupling constant will be a half of that at a low temperature where the rapid translational motion is absent.

(3) Since the Z' direction of the tetrahedral sites in the S group is parallel to the c axis, the quadrupole coupling constant will not be averaged by the rapid translational motion of the deuteriums. Consequently, the quadrupole coupling constant is approximately the same as that for the ordered β_1 form.

TABLE 3. CALCULATED eq, η AND CONFIGURATIONAL ENTROPIES FOR THE VARIOUS PROPOSED β_2 Ta_2D STRUCTURES

	$eq_{\beta 2}/eq_{\beta 1}$ [a]	η	S_c(e.u. mol^{-1})
L [b]	1/2	0	5.97
S [c]	1	0	4.20
L and S [d]	0	—	6.82

a) $eq_{\beta 1}$ is given by Eq. (5).
b) Random distribution in the L sites.
c) Random distribution in the S sites.
d) Random distribution in all sites.

The calculated eq, the asymmetry parameters, and the configurational entropies for the three proposed structures are shown in Table 3. It should be noted that the observed deuteron resonance line shape exhibits no quadrupole coupling constant change upon the $\beta_1 \rightarrow \beta_2$ phase transition, and that the most probable structure for the β_1 form is the PSSC ordered model. Then, from an inspection of the table, one can see that the distribution in the S sites seems to be the probable structure for the β_2 form. However, the calculated configurational entropy is far larger than the observed value, 0.7 e.u. mol^{-1}. In order to account for the large difference between the calculated and observed entropies, we must take some kinds of local order into consideration.

Local Order in the β_2 Form. The locally ordered structure which we will discuss in this section must satisfy the following three conditions; (1) the deuteron quadrupole coupling constant and asymmetry parameter of the β_2 form must be of the same order as the β_1 form; (2) in spite of the above condition, there must be no superlattice diffraction in the β_2 form, and (3) the configurational entropy of the β_2 form must be only 0.7 e.u. mol^{-1}. From condition (1), we see that the arrangement of Ta atoms around the deuterium atom is the same as that of the β_1 form. This means that the symmetry of the β_2 form must be orthorhombic. From condition (2), we see that the deuteriums must be distributed over all the tetrahedral sites in the S group with a quarter occupancy. This means that the symmetry of the β_2 form must be tetragonal. However, this tetragonality contradicts condition (1), while a quarter occupancy contradicts condition (3).

Let us try to account for the above contradiction. In the A222 space group, without considering the displacement of Ta ($4K$ positions), the $2a$(1/4 1/4 1/4, 1/4 3/4 3/4), $2b$(1/4 1/4 3/4, 1/4 3/4 1/4), $2c$(3/4 1/4 3/4, 3/4 3/4 1/4), and $2d$(3/4 1/4 1/4, 3/4 3/4 3/4) positions are all equivalent. In the ordered structure, the deuteriums are at the $2a$ positions and the Ta are displaced by $\pm x$. However, as the temperature increases, the preservation of the mutual positions of the deuteriums becomes difficult and probability of finding deuteriums in the $2b$, $2c$, and $2d$ positions becomes progressively larger. However, before the deuteriums are found to be statistically distributed over these sites, one may find a locally ordered structure. This consideration yields a concept of a domain structure which is constructed with four types of domains. The deuteriums in the domains are, of course, at the $2a$, $2b$, $2c$, and $2d$ positions. Since the domains are perfectly ordered internally, the configurational entropy is merely the entropy of the mixing of the domains. For one mole of Ta_2D, the number of domains is $N/(2r^3)$, where N is the Avogadro number, where r is a repeat number of a unit lattice per domain, and the number of complexions is $(N/(2r^3))!/((N/(8r^3))!)^4$ and $S_c = R\ln 4!/(2r^3)$. The probable value of r, which is determined so that the calculated value coincides with the experimental value of 0.7 e.u. mol^{-1} is 1.4. For such small domains, as Wallace[5] has pointed out, sharp superlattice diffractions do not develop and the diffraction pattern closely resembles that in which deuteriums are randomly distributed over the S sites. Therefore, we can assume that the above domain structure satisfies the three conditions simultaneously and seems to be the most probable structure. An example of the domain structure projected onto 100 plane is shown in Fig. 5.

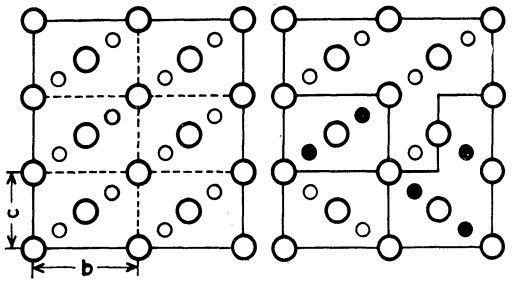

Fig. 5. Projection onto 100 plane of the ordered β_1 (left) and locally ordered β_2 form (right). Only Ta's at $x=0$ (opened large circles) are shown. D's are at $x=1/4$(small opened circles) and $x=3/4$ (small closed circles).

Deuterium Arrangement in α Ta_2D. The quadrupole coupling constant of this form is too small to be detected. This fact can be accounted for if the deuteriums are undergoing a rapid translational motion over all available tetrahedral sites (L and S sites). The configurational entropy calculated from this structure is 6.82 e.u. mol^{-1}. On the other hand, Saba *et al.*[4] have shown that the configurational entropy of this form is 4.9 e.u. mol^{-1}, which does not change even at 573°K. This indicates that the deuteriums are not randomly distributed over all the tetrahedral sites, but are dis-

tributed in a manner which retains some kinds of local order. However, in considering such a locally ordered structure, it should be taken into account that (1) the crystal is cubic and (2) the quadrupole coupling constant is averaged to zero. These conditions require that, in a locally ordered domain, there must be three different equally abundant sites, whose Z' directions are parallel to the a, b, and c axes respecitvely. It is possible to imagine such a domain structure without a loss of crystal symmetry. However, since it is difficult to interpret why such domain structure is energetically stable, we will not discuss further this problem.

Electric Field Gradient Calculation. In the previous section, we have used a simple electrostatic model in which the electric potential from the ions is screened by the conduction electrons around the ions. However, we have left the constant, K, and the electric charge on the ions underemined. In this section, we will discuss these parameters.

It has been shown that when a hydrogen enters the metal, it loses most of its electron cloud to the conduction band or to the metal ions. The ^{139}La magnetic resonance study of La–H[13] system has shown that the EFG at the La ion due to the defect of hydrogen ions can best be calculated by the assumption of a positive charge on the hydrogen ion. However, the relatively large negative proton Knight shift in the Ti–H system[18] has shown that the hydrogen does not lose its electron completely in this system. Schreiber and Graham[19] have suggested, from the zero proton Knight shift in the Ta–H, Nb–H, and V–H systems, the existence of bare protons in these systems. The proton relaxation times of Ta–H[17] and Nb–H[20] systems have shown no contribution of conduction electrons to their relaxation mechanisms. Therefore, the assumption of a positive charge on the interstitial deuterium ions is a good approximation.

In compensation for a positive charge on hydrogen ions, a negatively ionized metal ion model has been presented.[14] However, this assumption is inconsistent in its use of a screened potential and also contradicts the pulsed NMR result[21] that the hydrogen diffusion activation energy is independent of the hydrogen concentration. We assume that the effect of electrons removed from the interstitial hydrogen atoms is merely to change the conduction electron density slightly and that this effect has no influence on the net charge of the Ta ions.

The values of K for Cu, Ag, and Al have been calculated to be 1.72 to 1.81×10^8 cm^{-1}. Due to the r_{ij}^{-3} and $\exp(-Kr_{ij})$ terms in Eq. (2), the summation in Eq. (1) easily converges. The computation has been made over 68 Ta and 29 deuterium ions within the sphere of radius of $R=\sqrt{69}\,a_0/4$. With $a_0=3.37$, $c/a=1.008$, and displacement parameter $x=0.012$, some combinations of K and Z_{Ta} which have been so determined as to the calculated quadrupole coupling constants agree with the observed value, 33.9 KHz, are as follows;

Z_{Ta}	K	η
5	1.75×10^8 cm^{-1}	0.235
4	1.54×10^8 cm^{-1}	0.186
3	1.47×10^8 cm^{-1}	0.128

The dependence of η on Z_{Ta}, of course, comes from the contribution on the Ta ion to the EFG. Since the observed asymmetry parameter lies between 0.25 to 0.15, 4 to 5 charge on the Ta ion seems to be plausible. However, if the deuteriums do not lose their electron cloud completely, a +5 charge on the Ta ion may be more realistic.

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Appendix

Analysis of Powder Pattern for Asymmetric Field Gradient.

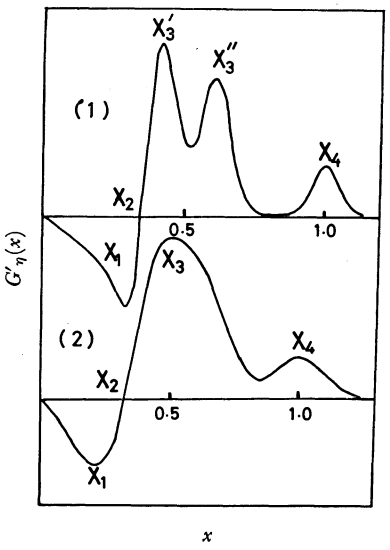

Fig. 6. Calculated powder patterns for $\eta=0.25$.
(1) $\sigma=0.05$ (2) $\sigma=0.1$

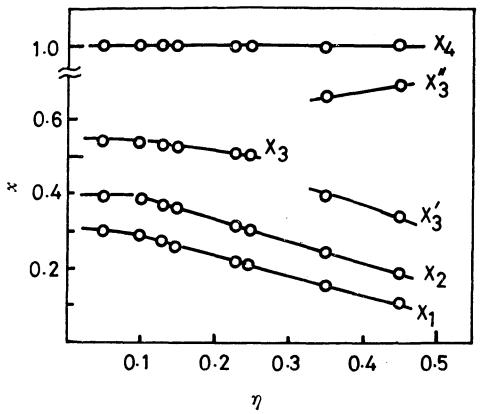

Fig. 7. Plots of x_1, x_2, x_3 (x_3', x_3'') and x_4 against η for $\sigma=0.1$ case.

18) B. Stalinski, C. K. Coogan, and H. S. Gutowsky, *J. Chem. Phys.* **34**. 1191 (1961).
19) D. S. Schreiber and L. D. Graham, *ibid.*, **43**, 2573 (1965).
20) D. Zamir and R. M. Cotts, *Phys. Rev.*, **134**, 666 (1964).
21) C. Korn and D. Zamir, *J. Phys. Chem. Solids*, **31**, 489 (1970).

The first-order powder pattern of one satellite for asymmetric field gradient, $P_\eta(x)$, is defined in Ref. (9) page 342. If the individual lines are assumed to be the form as,

$$f(x) = \exp[-(x-x')^2/2\sigma^2] \tag{1'}$$

where $x=(\nu-\nu_0)/(3e^2qQ/4h)$. The resultant shape function, $G'_\eta(x)$ (derivative), is given

$$G'\eta(x) = \int_{-1}^{1}(x-x')[P(x')+P(-x')]\exp[-(x-x')^2/2\sigma^2]\mathrm{d}x' \tag{2'}$$

Examples for $\eta=0.23$ are shown in Fig. 6. We define x_1, $x_3(x_3', x_3'')$ and x_4 as derivative maxima (minimum) and x_2 as derivative zero. As shown in Fig. 7, x_1 and x_2 are very sensitive to η, x_1 and x_2 may be used to obtain η. Quadrupole coupling constant is most accurately determined by measuring x_4 which is very insensitive to η and σ. When η is large enough or σ is small enough to be able to observe the separation between x_3' and x_3'', η may be very easily obtained by comparing $(x_3''-x_3')/(x_4-x_3'')$ against η as shown in Fig. 8.

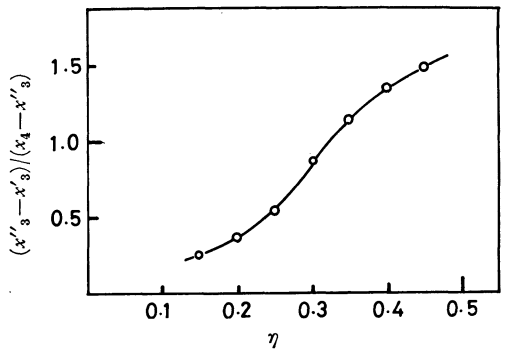

Fig. 8. A plot of $(x_3''-{}_3x')/(x_4-x_3'')$ against η for $\sigma=0.05$ case.