Deuteron and Niobium-93 Magnetic Resonance Studies of the Nb-D System. Comments on the Effects of Interstitial Impurities

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The deuteron and niobium magnetic resonance in the Nb–D system have been measured over a wide range of deuterium concentrations. It has been found that the order-disorder ($\beta \rightarrow \alpha$) phase transition temperature depends on the small amount of interstitial impurities as well as on the concentration of the deuterium. From the concentration dependency of deuterium (Nb) in the α phase, one can determine the amount of deuterium (Nb) in the β phase coexisting with that in the α phase. On the basis of this finding, a tentative Nb–D phase diagram has been proposed. It has been confirmed that the interstitial impurities decrease the deuterium concentration of the β phase which is in equilibrium with the α phase. The niobium signal intensity has been found to be greatly reduced by the interstitial oxygen and other impurities, while the line width is not affected. For the interpretation of these findings, a simple model has been proposed in which only the interstitial atoms, which are present within the spherical sphere of a critical radius, r_c, from a niobium atom, eliminate the niobium resonance by means of the second-order quadrupole interaction.

Numerous studies have been made of the Va metal–Hydrogen system.¹⁾ In these systems, the number of interstitial sites is greater than that of the interstitial hydrogen atoms, and a ninteresting phenomenon related to the order-disorder phase transition²⁾ has been reported. By the method of neutron diffraction, Somenkov *et al.*³⁾ have determined the atomic arrangement in niobium deuteride with a composition close to the equiatomic ratio (0.88~0.95 D/Nb) and have found that, at room temperature, the arrangement of deuterium atoms is ordered, filling four tetrahedral sites of the face-centered orthorhombic cell of niobium metal. As the temperature increases, the arrangement of deuteriums becomes disordered. They proposed two possible structures for the high-temperature form (α form). One of the structures, however, seems to be unlikely from the NMR point of view, as will be discussed below.

In the previous paper (hereafter denoted as I),⁴⁾ the present author has shown that the deuteron quadrupole splitting spectrum in the ordered β Ta_2D can be accounted for if deuteriums occupy tetrahedral sites with the largest principal component of the electric-field gradient (EFG) parallel to the c axis. In I, it has also been shown that the sharp single resonance line observed for the disordered α Ta is an indicative of the random distribution of deuterium in the tetrahedral interstices of the body-centered cubic metal.

The Nb–D system, like the Ta–D system, shows a spectrum of quadrupole splitting in its ordered state.⁵,⁶⁾ This is consistent with the existence of superlattice diffractions³⁾ in the same system. In spite of the resemblance of the Nb–D and Ta–D systems in their quadrupole splitting spectra and the superlattice diffraction patterns, there are considerable differences between the two systems. For instance, the deuteride phase (β phase) of the Ta–D system, which is in equilibrium with the metallic phase (α phase), has the composition of Ta_2D, while that for the Nb–D system has a composition close to Nb_4D_3.⁷,⁸⁾ The Ta–D phase diagram, as determined by X-ray measurement,⁹⁾ is consistent with the proton¹⁰⁾ and deuteron magnetic resonance⁴⁾ results. However, the Nb–H phase diagram, as determined by means of the proton and niobium magnetic resonance¹¹⁾ is different from the phase diagram as determined by X-rays and by thermal analysis.⁸⁾ It is one of the purposes of this paper to reexamine the phase diagram of the Nb–D system.

Together with the tendency to deuteride formation, Va metals have a strong affinity to oxygen. Commercially-available niobium metal powder usually contains about 0.3~0.4 wt% oxygen. In this paper, we will show that discrepancies in the composition of the ordered phase, the phase-transition temperatures, and the solubility of hydrogen in the metallic phase are due to differences in the contents of oxygen and other interstitial impurities.

Experimental

Two types of niobium specimens with different oxygen contents were used for the preparation of deuterides. One specimen was a powdered niobium obtained from Herman Stark; it contained about 3900 ppm oxygen, 560 ppm nitrogen, and 200 ppm carbon (hereafter denoted as the S–II series). This powdered niobium metal was purified by using a electron-beam melting furnance. The purification was carried out

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1) For reviews, see G. G. Libowitz, *J. Nucl. Mater.*, **2**, 1 (1960). H. Asano and M. Hirabayashi, *Buturi*, **26**, 273 (1971).

2) W. G. Saba, W. E. Wallace, H. Sandmo, and R. S. Craig, *J. Chem. Phys.*, **35**, 2148 (1961).

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4) K. Nakamura, This Bulletin, **45**, 3356 (1972).

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7) G. Brauer and R. Hermann, *Z. Anorg. Chem.*, **274**, 11 (1953).

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four times. The purified ingot was rolled to make a foil 0.05 mm thick. The final oxygen content, as determined by the inert gas fusion method, was 12±2 ppm. The other interstitial impurities were 30 ppm carbon and 17 ppm nitrogen. This foil was used to prepare deuterides of the S–I series. The deuteration was carried out as follows. The niobium specimen was placed in a quartz tube and subjected to thermal treatment in a vacuum of 1.2×10^{-5} mmHg at about 800 °C. Then, a known amount of deuterium gas as purified by means of Hydrogen Purifier[12] (Pd membrane method), was introduced, after which the sample was cooled to 150 °C and kept about two hours. The deuteride foil was then crushed to powder. In this deuteration process, the oxygen content increased from 12 ppm to 70~80 ppm for the S–I series, and from 3900 ppm to 4100~4500 ppm for the S–II series. The accuracy in the composition determination was within ±0.4%. The D/Nb atomic ratios of the deuterides examined were as follows:

S–I series: 0.236, 0.347, 0.480, 0.532, 0.587, 0.612, 0.699, 0.715, 0.738, 0.746, 0.796, 0.804, 0.822, 0.855, 0.899, 0.945.

S–II series: 0.232, 0.340, 0.426, 0.562, 0.646, 0.727, 0.807, 0.837, 0.874, 0.890.

The deuteron and niobium-93 resonance measurements were made by using a Varian VF-16 wide-line NMR spectrometer, operating mainly at 6.53 MHz for the deuteron and at 10.47 MHz for the niobium resonance. In some cases, other frequencies were employed to see the effect of the magnetic-field strength. The temperatures of the samples were controlled with a Varian variable-temperature accessory.

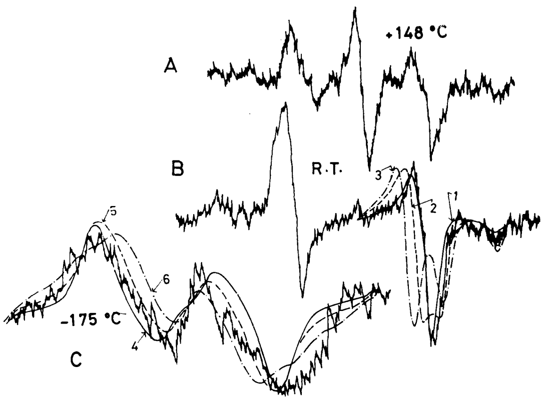

Fig. 1. Observed deuteron resonance spectra of $\mathrm{NbD}_{0.855}$ (S-I series). Smoothed curves (1—6) are drawn with $e^2qQ/h=$ 32.8 KHz and with various values of asymmetry parameters, η, and individual line width, σ.

	$\sigma/(3e^2qQ/4h)$	a
1	0.05	0.03
2	0.05	0.15
3	0.05	0.25
4	0.15	0.13
5	0.15	0.23
6	0.15	0.40

Results

Deuteron Resonance at Room Temperature. The room-temperature deuteron resonance spectra of the Nb–D system resemble those of the Ta–D system.[4] In the case of a D/Nb atomic ratio of less than ≈0.65, the powder pattern consists of two parts; one is a sharp, single line located at the center of the spectrum, and the other is a pair of lines which are characteristic of a nuclei with $I=1$ in the presence of an approximately axially-symmetrical EFG. However, for the samples with D/Nb atomic ratios larger than ≈0.65, the central line becomes unobservable. According to the Nb–H phase diagram (Fig. 2), the central line can be attributed to the deuterium of the α phase and the satellites to the β-phase deuterium.

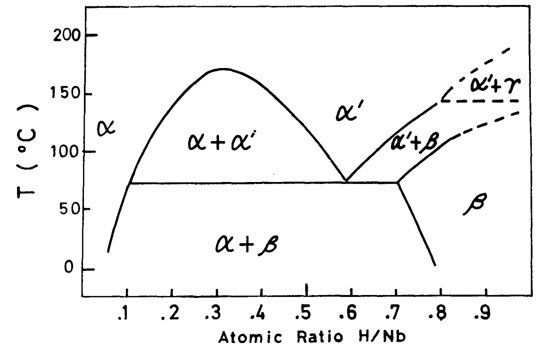

Fig. 2. The phase diagram of Nb–H system[8]

Table 1. Room temperature's deuteron quadrupole coupling constants, e^2qQ/h, and asymmetry parameters for the Nb–D system (S–I and S-II series)

	D/Nb	e^2qQ/h (KHz)[a]	η[b]
S-I	0.945	31.8	0.07
	0.822	32.8	0.04
	0.796	33.2	0.04
	0.738	33.4	0.03
	0.612	33.2	0.03
S-II	0.890	31.2	0.05
	0.874	31.6	0.04
	0.837	31.6	0.04
	0.727	32.2	0.03

a) The mean errors in the e^2qQ/h are less than 0.3 KHz
b) The mean errors in the η are less than 0.02.

A detailed analysis of the powder pattern for the nuclei with $I=1$ in the presence of an asymmetric-field gradient has been shown in the Appendix of I. The quadrupole coupling constants and the asymmetry parameters obtained by using the analytical method of I are shown in Table 1. The observed quadrupole coupling constants and the asymmetry parameters in the same series are almost concentration-independent up to ≈0.822 D/Nb (S-I). However, slight decreases in the quadrupole coupling constants are observed in the highest deuterium-concentration range for both series. The quadrupole coupling constants of the Nb–D system (S-II) containing oxygen are smaller by about 0.6~1.0 KHz than those of the oxygen-free Nb–D system (S-I).

Deuteron Resonance and Phase Transition above Room Temperature. As the temperature of the sample increased from room temperature, the apparent signal intensity of the central line began to increase and that of the satellite line began to decrease, indicating that the β→α phase transition occurred. Since the line-

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[12] Japan Pure Hydrogen Co., Ltd.

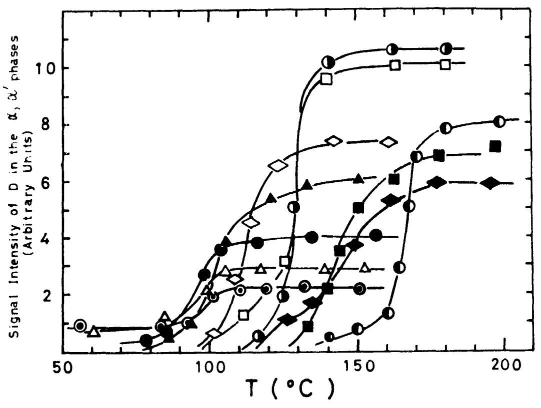

Fig. 3. Temperature dependence of the deuteron central line intensity of the S–I series.

D/Nb	D/Nb	D/Nb
◎ 0.236	▲ 0.587	◆ 0.855
△ 0.347	◇ 0.699	■ 0.899
● 0.480	□ 0.738	◐ 0.945
	◑ 0.804	

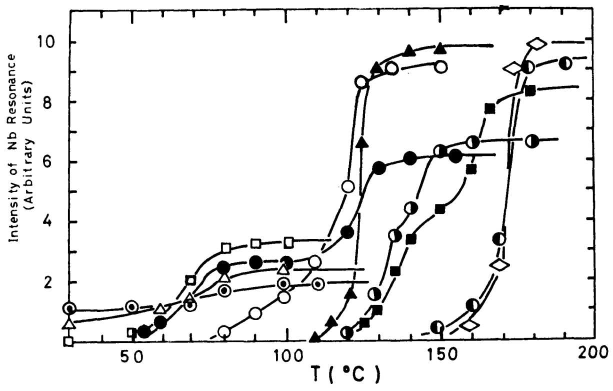

Fig. 4. Temperature dependence of the deuteron central line intensity of the S–II series.

D/Nb	D/Nb
⊙ 0.232	▲ 0.727
△ 0.340	◑ 0.807
□ 0.426	■ 0.837
● 0.562	◐ 0.874
○ 0.646	◇ 0.890

width of the central line above room temperature is mainly determined by the bulk magnetization of the deuterides,[11] and since the line-width is constant above room temperature ($\Delta H_{\mathrm{msl}} \approx 0.5$ G at 10 KG.), the signal intensity (apparent peak to peak intensity $\times 1/T$) of the central line is taken as proportional to the concentration of the deuterium atoms in the α phase. In Figs. 3 and 4, the signal intensities of the central lines are shown as a function of the temperature. These figures suggest that the phase-transition temperatures of the S-I series are higher than those of the S-II series by about 25 to 10 °C. The following have been noted for the two series.

S-I series: As may be seen in Fig. 3, a sharp phase transition occurs at three different temperatures, about 95, 130, and 170 °C, although some gentle phase-transition curves can be seen at the intermediate temperatures for the samples with intermediate compositions, which will be discussed below. For $NbD_{0.587}$, which is in the $\beta+\alpha$ region at room temperature, the $\beta+\alpha\rightarrow\alpha$ phase transition is initiated at about 90 °C and is finished at a temperature close to the $\beta\rightarrow\alpha$ phase-transition temperature of $NbD_{0.738\sim0.804}$ ($\approx$130 °C). The existence of such a broad two-phase region may be related to the presence of two types of α forms, α and α'. The solubility of deuterium in the α' form is greater than that in the α form. The fact that two types of α forms exist is consistent with the findings in the Nb–H phase diagram.[8]

As has been mentioned above, gentle phase-transition curves are observed with the samples of $NbD_{0.855}$ and $NbD_{0.945}$ in the intermediate region between curves of $NbD_{0.855}$ and $NbD_{0.945}$. This indicates that there is a relatively broad $\beta+\alpha'$ region in the temperature range from 130 to 170 °C. Thus, it may be concluded that, in this two-phase region, the β phase, which is in equilibrium with the α' phase, must have a composition larger than 0.899 D/Nb. For $NbD_{0.899}$, the $\beta\rightarrow\beta+\alpha'$ phase-transition begins at a temperature close to the $\beta\rightarrow\alpha'$ phase-transition temperatures of $NbD_{0.738\sim0.804}$. The $\beta+\alpha'\rightarrow\alpha'$ phase transition for the same sample is finished at a temperature close to the $\beta\rightarrow\alpha'$ phase transition temperature of $NbD_{0.945}$. These facts may be well interpreted by assuming that the β phase consists of two types of β forms. This deuteron magnetic resonance behavior shows a good agreement with the niobium resonance, which will be discussed later.

S–II series: The phase-transition behavior of the S–II series is approximately analogous to that of the S–I series. However, the following points of disagreement are observed. a) The $\beta+\alpha\rightarrow\alpha+\alpha'$ phase-transition temperatures from $NbD_{0.232}$ to $NbD_{0.426}$ are lower by about 20 to 25 °C than those of the corresponding deuterides of the S–I series. The $\beta\rightarrow\alpha'$ phase-transition temperature of $NbD_{0.727}$ is lower by about 10 °C than that of the corresponding deuteride of the S–I series. b) The compositions where the sharp $\beta\rightarrow\alpha'$ ($\approx$130 and $\approx$170 °C) phase transitions occur are lower by about 0.06 D/Nb than those of the S–I series.

Deuteron Resonance below Room Temperature. As the temperature of the sample decreased, the signal intensity of the α form decreased, until finally it vanished in the temperature range from −10 to −70 °C. The quadrupole coupling constants and the asymmetry parameters measured at −50 °C show no significant change as compared with those at room temperature. As the temperature decreased from −70 °C, the satellite lines became broad; this broadening ended at about −120 °C. This is consistent with the temperature dependence of the proton line width in the Nb–H system.[13] In Fig. 1-(C), three calculated line shapes with different asymmetry parameters are shown. The value of the line-width, σ, is taken from the D–Nb dipole-dipole interaction.

Niobium Magnetic Resonance. At room temperature, the observed niobium magnetic resonance intensity is roughly proportional to the concentration of the cubic α phase, which coexists with the unobservable orthorhombic β phase. This is consistent with the findings

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[13] B. Stalinski and O. J. Zogal, *Bull. Acad. Poln. Sci. Ser. Chem.*, **13**, 397 (1965).

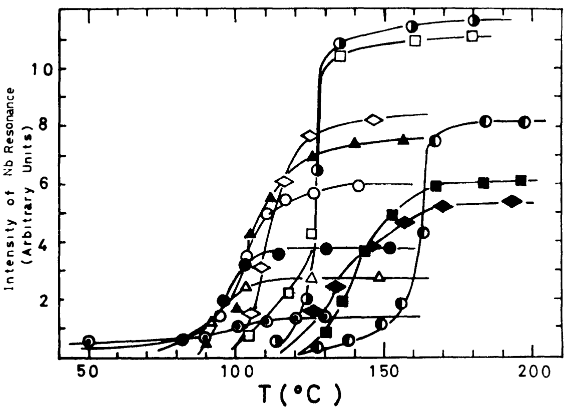

Fig. 5. Temperature dependence of the niobium-signal intensity of the S–I series. The assignments of the marks in the figure are the same as those of Fig. 3.

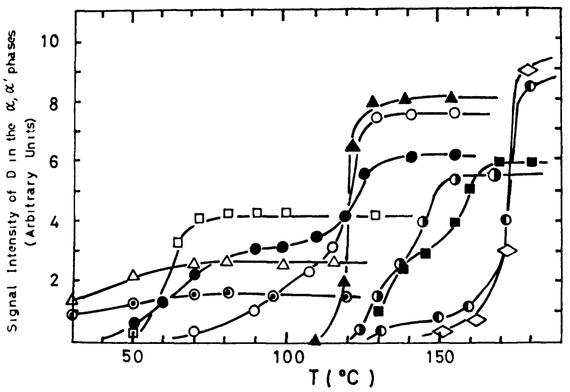

Fig. 6. Temperature dependence of the niobium-signal intensity for the S–II series. The assignments of the marks in the figure are the same as those of Fig. 4.

on the niobium magnetic resonance in the Nb–H system.[11] Since the variation in the line-width of the α Nb with the temperature is very small as compared with the variation in the apparent signal intensity, the signal intensity may be useful for the investigation of the phase-transition behavior of the Nb–D system. The temperature dependences of niobium-signal intensities shown in Figs. 5 and 6 agree well with the temperature dependence of the deuteron-signal intensities.

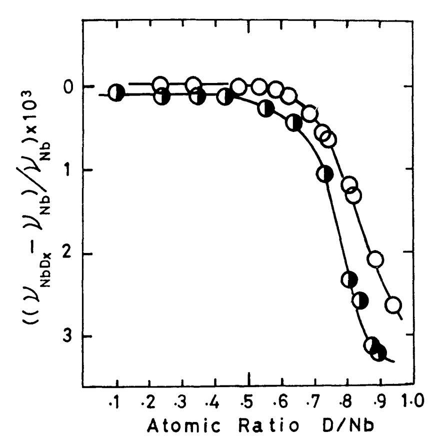

Fig. 7. Concentration dependence of the niobium resonance shift in the NbD$_x$ relative to that in the pure Nb metal.
○: S–I series ◑: S–II series

The concentration dependence of the niobium Knight shift change measured at +180 °C is shown in Fig. 7. The variation in the niobium Knight shift up to 0.7 D/Nb agrees well with the previous results.[11] However, in this case, sharp decreases in the Knight shift are observed in the concentration range from 0.7 D/Nb to the highest concentration studied for both series.

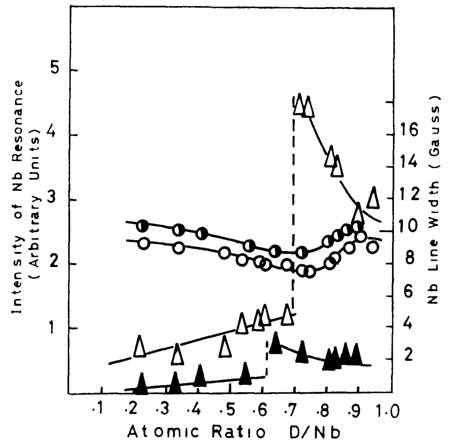

Fig. 8. Concentration dependence of niobium-signal intensity (△ S–I series, ▲ S–II series) and niobium line-width (○ S–I series, ◑S–II series).

The concentration dependence of the niobium-signal intensity shown in Fig. 8 is not so simple as has been indicated in one previous paper.[11] The niobium resonance intensity of Nb metal is affected strongly not only by its heat treatment, but also by the small amount of interstitial impurities. In the Nb–D system, the niobium resonance intensity decrease due to the interstitial impurities is observed for the S–II series, while the line-width increase is unexpectedly small.

A deuterium concentration dependence of the niobium-signal intensity is also observed in this study. A sharp, discontinuous increase in the niobium-signal intensity is observed at about 0.73 D/Nb for the S–I series. However, the line-width change at this concentration is small and gradual. At this temperature, niobium deuteride is in the cubic phase for all the deuterium concentrations. Thus, these sharp and discontinuous intensity changes can not be interpreted in terms of the present phase diagram.

Discussion

Probable Deuterium Arrangement in the β Form. As has previously been shown, the deuteron quadrupole splitting spectra at low temperatures, where the dipolar width of an individual line is assumed to be equal to the rigid lattice one, are essentially the same as that at room temperature. This fact shows that the deuteron quadrupole coupling constant is independent of the translational motion of deuteriums; that is, all the positions occupied by deuterium atoms must be equivalent. For the face-centered orthorhombic cell (a= 4.83, b=4.89, and c=3.44 Å),[7] of the β form, only the following 8 positions are equivalent: 1/4 1/4 1/4, 1/4 1/4 3/4, 1/4 3/4 1/4, 1/4 3/4 3/4, 3/4 1/4 1/4, 3/4

1/4 3/4, 3/4 3/4 1/4, and 3/4 3/4 3/4. This consideration confirms the finding of an recent neutron diffraction study[3] that the deuteriums are in the 2a (1/4 1/4 1/4, 3/4 3/4 3/4) and 2b (3/4 1/4 1/4, 1/4 3/4 3/4) positions of the face-centered orthorhombic cell (space group, Pnnn).

It is of particular interest to see the concentration dependency of the quadrupole coupling constant and the asymmetry parameter of the β form. An X-ray diffraction study[14] of the niobium hydride phase has shown that both the distortion from cubic symmetry and the increase in the lattice parameters occur as the concentration of hydrogen increases from $\approx$0.7 H/Nb. The former effect may increase the asymmetry of the EFG, while the latter decreases the principal component of the EFG. On the other hand, although the electrostatic potential from the positively-charged interstitial deuterium atoms is fairly screened,[16] the increase in the deuterium concentration may increase the quadrupole coupling constant. From a simple electrostatic calculation,[4] this effect can also be seen to increase the asymmetry of the EFG. The experimental results shown in Table 1 exhibit a significant increase in the asymmetry parameters of the S–I series. However, no significant change in the asymmetry parameters is observed for the S–II series. Thus, from the significant change in the quadrupole coupling constants, it may be concluded that the electrostatic potential from the interstitial deuteriums is almost screened and that the effect of lattice expansion is dominant in this case.

Deuteron Resonance Line Shape and Deuterium Arrangement in the Low-temperature Region. Somenkov *et al.*[15] have shown that the partially-ordered deuteride which was found in the solid solution of 3 atomic percent deuterium becomes ordered at -100 °C. The composition of the ordered phase was found to be Nb_4D_3. The crystal has a cell which is double in all directions with respect to the ordered $NbD_{1.0}$ cell. The structure is shown in Fig. 9. An examination of the figure will show that the unit cell consists of four $NbD_{1.0}$-type ordered cells and four Ta_2D-type ordered cells. Since the EFG at the deuterium atom in the Ta_2D-type ordered cell is characterized by a relatively large asymmetry parameter ($\simeq$0.24),[4] the EFG of the ordered Nb_4D_3 is considered to have an asymmetry parameter larger than that for the room-temperature form.

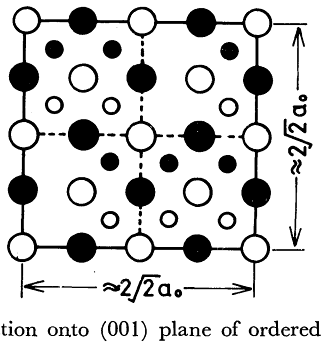

Fig. 9. Projection onto (001) plane of ordered Nb_4D_3 structure.[15] Nb's are at $z=0$, 1/2 (large open circles) and at $z=1/4$, 3/4 (large full circles). D's are at $z=1/8$, 5/8 (small open circles) and at $z=3/8$, 7/8 (small full circles).

In Fig. 1-(C), the calculated line shapes for three values of asymmetry parameters are shown. Because of the poor signal-to-noise ratio of the observed spectrum, it is difficult to decide which one of the calculated line shapes fits the observed one. Another difficulty in the decision may lie in the approximate-line-shape calculation, for we have disregarded the increase in the EFG due to lattice contraction and the angle dependency of the individual line-width.

Nb–D Phase Diagram as Determined by Deuteron and Niobium Magnetic Resonance. The Nb–H phase diagram proposed by Walter and Chandler[8] is shown in Fig. 2. Apart from the difference in the phase-transition temperature, the essential features of this phase diagram may be used in discussing the Nb–D system. The following features are in accord with our results:

1) At room temperature, the α phase is between 0 and $\simeq$0.1 H/Nb, while $\alpha+\beta$ is between $\simeq$0.1 and $\simeq$0.75 H/Nb.

2) In the concentration range of less than 0.5 H/Nb, the $\alpha+\beta\rightarrow\alpha+\alpha'$ phase transition occurs at about 60 °C, lower by about 20~30 °C than that for the Nb–D system.

3) In the concentration range between 0.75 and 0.85 H/Nb, the phase transition proceeds according to $\beta\rightarrow\beta+\alpha'\rightarrow\alpha'$.

However, the following aspects of the phase transition behavior can not be interpreted in terms of the Nb–H phase diagram:

4) $\alpha+\beta\rightarrow\alpha'+\beta\rightarrow\alpha'$ two-step phase transition for $NbD_{0.532\sim0.699}$.

5) $\beta\rightarrow\alpha'$ sharp phase transition for $NbD_{0.738\sim0.804}$.

6) $\beta\rightarrow\alpha'$ one-step phase transition for $NbD_{0.945}$.

7) Between 0.7 and 0.8 H/Nb, the Nb–H phase diagram shows that the phase transition proceeds according to $\beta+\alpha\rightarrow\beta\rightarrow\beta+\alpha'\rightarrow\alpha'$. However, if we take into consideration the neutron diffraction[3,15] and the heat capacity findings[9] that the β phase is in an ordered state and that the α phase is in a disordered state, the $\beta+\alpha\rightarrow\beta$ phase transition may be thought to be a disorder-order phase transition. Therefore, the $\alpha+\beta/\beta$ boundary line must be perpendicular to the X axis (composition axis) or, at least, must be a rising gradient.

As has been described previously, the existence of two sharp phase transitions, 5) and 6), can be accounted for if the β phase consists of two types of β forms with similar structures. However, this assumption contradicts the X-ray diffraction finding[14] that the change in the lattice parameters in the β-phase region (0.7 to 0.9 H/Nb) is continuous. A tentative Nb–D phase diagram which is consistent with both our NMR and the X-ray

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[14] C. Wainright, A. J. Cook, and B. E. Hopkins, *J. Less-Common Metals*, **6**, 362 (1964).

[15] V. A. Somenkov, V. F. Petrunin, S. Sh. Shil'shtein, and A. A. Chertkov, *Soviet Physics-Crystallography*, **14**, 522 (1970).

[16] N. F. Mott and G. H. Johnes "Theory of the Properties of the Metals and Alloys," Oxford Univ. Press, New York (1936), p. 86.

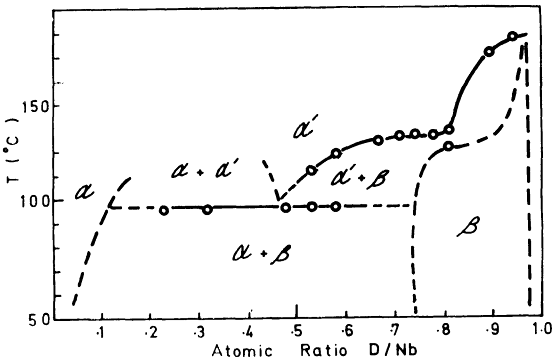

Fig. 10. Proposed phase diagram for Nb–D system.

diffraction results[14] is shown in Fig. 10. This diagram is quite different from any phase diagrams for a binary system ever published. In this phase diagram, the change in the $\alpha'+\beta/\beta$ boundary against the deuterium concentration occurs in one step, as if there are two types of β phases. However, this one-step change in the $\alpha'+\beta/\beta$ boundary may be explained by the schematic free energy-composition diagram shown in Fig. 11.

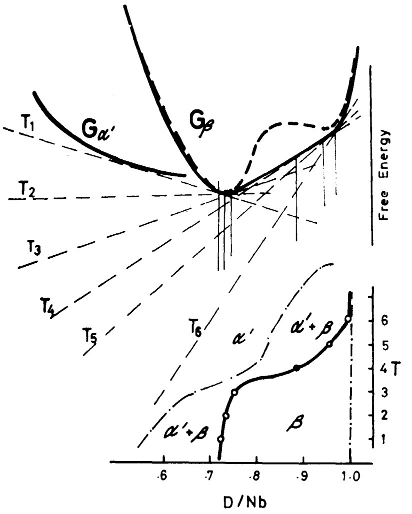

Fig. 11. Common tangents to the schematic free energy-composition curves for the β and α' phases at temperatures from T_1 to T_6 (upper). Only G_{α}' for T_1 is shown. Dotted line shows the free energy curve for the case where two β phase coexists. $\beta+\alpha'/\alpha'$ bundary derived from the upper diagram is shown below.

In Fig. 11, the $\alpha'+\beta/\beta$ boundary may be determined by a common tangent with the free energy-composition curves for the β and α' phases ($G_{\alpha'}$ and G_{β}). For the sake of simplicity, the shape for $G_{\beta'}$ is assumed to be temperature-independent. Since the β phase is an ordered one, while the α phase is a disordered one, the change in the gradient of the common tangent with the increase in the temperature from T_1 to T_6 must be positive. If the G_{β} curve is almost linear between $\simeq$0.7 to $\simeq$1.0 D/Nb, a sharp change in the $\alpha'+\beta/\beta$ boundary may be observed from T_3 to T_5. The resultant phase diagram closely resembles that in which two β phases of different compositions coexist.

Effect of Interstitial Impurities on Niobium Resonance Intensities.[17] In the course of this investigation, we have found large differences between the properties of niobium deuterides prepared from electron beam-melted niobium metal (S–I series) and those prepared from commercially-available powdered niobium metal (S–II series). The major interstitial impurity in the S–II series is oxygen. One of the most outstanding phenomena is the niobium signal intensity reduction in the S–II series. As is shown in Fig. 8, the addition of about 2.3 atomic percent (0.4 wt%) of oxygen reduces the intensity to about 10~40% of that of oxygen-free deuterides. If the dissolved oxygen is used to form a NbO-type oxide, the reduction of the intensity will be of an order of only a few percent. Since the observed reduction is far larger than 2.3%, then, most of the dissolved oxygen atoms must be randomly distributed over the interstices of the metal. This is possible in view of the relatively large solubility of oxygen in the metallic niobium.[18]

In Fig. 8, the maximum resonance intensity is observed for $NbD_{0.738}$ of the S–I series. The intensities of the $NbD_{0.236\sim0.587}$ of the same series are about 13~17% of its maximum intensity. If the satellite lines are eliminated by the first-order quadrupole interaction, and if the observed resonance is due to the $1/2\leftrightarrow-1/2$ transition only, the theoretical intensity should be 15.1% of its maximum intensity. Thus, the intensity loss of the S–I series seems to be due to the first-order quadrupole interaction.

The mechanism of the intensity loss due to the addition of interstitial impurities is somewhat different from that of the S–I series. For samples with D/Nb ratios lower than $\approx$0.5, where the observed resonance is due to the $1/2\leftrightarrow-1/2$ transition only, the reduction of intensity due to the addition of interstitial impurities must be caused by the second-order quadrupole interaction. A comparision of the resonance intensities of the S–I and S–II series shows that the intensity loss of the S–II series is about 87—83%. However, the line-width increase of the same series is less than 10% and the change in the line shape is small. This is contrary to what might be expected from a consideration of the second-order line broadening of the central line.[17]

To account for the above contradiction, we will present a simple model for the intensity loss due to the interstitial oxygen. This model is similar to that proposed by Bloembergen and Rowland[19] for the Cu–Zn substitutional alloy. Since the major impurity is oxygen, it is not unreasonable to confine the discussion to a case where interstitial oxygen is dominant. Consider that there are two niobium atoms and N interstitial sites accessible for oxygen in a unit cell. If the atomic concentration of oxygen is C, the probability

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[17] As for static quadrupole broadening in metals, refer to M. H. Cohen and F. Reif, "Solid State Physics Vol. 5", Academic Press, New York (1957), pp. 365—420.

[18] A. Taylor and N. J. Doyle, *J. Less-Common Metals,* **13**, 313 (1967).

[19] N. Bloembergen and J. J. Rowland, *Acta Met.,* **1**, 731 (1953).

that an interstitial site is occupied by an oxygen atom is $C/(N/2)$. We assume that oxygen atoms within a sphere of a critical radius, r_c, from a given niobium atom casuse a field gradient sufficiently large to make the niobium resonance unobservable. The number of interstitial sites, n_c, within a radius of r_c is $(4\pi/3)\cdot(r_c/a_0)^3\cdot N$. Therefore, $(1-C/(N/2))n_c$ is the fraction of niobium atoms whose resonance is observable.

To calculate n_c, we must take into consideration the intensity loss due to the small line broadening. The fraction of niobium resonance observable has been calculated to be about 0.21～0.28. The number of interstitial sites in a unit cell is 12 for tetrahedral occupation and 6 for octahedral occupation. With an atomic fraction of oxygen of 0.024, and with a fraction of niobium observable of 0.24, n_c and r_c/a_0 have been calculated; these values are listed in Table 2. It should be noted that there are small amounts of other interstitial and substitutional impurites, and that the calculated r_c values are the upper limits.

TABLE 2.

	N	n_c	r_c/a_0
Tetra	12	328	1.87
Oct	6	168	1.88

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