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The Structure of Ordered β V_2D as Determined by Means of the Deuteron Magnetic Resonance

Keikichi NAKAMURA

National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153

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According to the V–D phase diagram,[1,2] there are three types of ordered phases: β V_2D, $\delta(\alpha'')$, and $\gamma(\alpha''')$ V_4D_3. The β form is body-centered tetragonal, with $c_0/a_0 \simeq 1.1$, and it is stable up to $+140$ °C. The δ and γ forms are pseudocubic and stable from -60 to -120 and below -120 °C respectively.

We have measured the deuteron magnetic resonance of the V–D system over wide ranges of the deuterium concentration and the temperature. The results confirm the published V–D phase diagram.[1,2] The deuteron quadrupole coupling constants have been measured as 68.6 ± 1.2 KHz (R.T.) for β V_2D and 37.5 ± 0.4 KHz (-130 °C) for γ V_3D_4. The asymmetry parameters were approximately zero for both forms. These values agree well with the recent NMR results.[3] The observed deuteron quadrupole coupling constants and the asymmetry parameter of δ, γ V_4D_3 are approximetely the same as those for β Nb_4D_3. In view of this fact and the similarity of neutron diffraction pattern between γ V_4D_3 and β Nb_4D_3,[4] it may be assumed that the deuteriums in γ V_4D_3 occupy tetrahedral intersticies such as those in the β Nb_4D_3.

The deuteron quadrupole coupling constant of β V_2D is roughly twice those of γ V_4D_3, β Nb_4D_3,[5] and β Ta_2D[6,7]. The c_0/a_0 ratio of β V_2D is about 1.1, which is different from the pseudocubic character of the other forms, — e.g., 1.008 for Ta_2D. In spite of the relatively large lattice expansion along the c axis, the asymmetry parameter is approximately zero. This is comparable to that of β Ta_2D ($\eta \simeq 0.24$).[6,7] These considerations clearly indicate the site of deuterium in β V_2D. Firstly, the EFG of the site must be symmetry with respect to the c axis. Secondly, the deuterium must repel the two nearest-neighboring vanadium atoms along the c axis so as to deform the cubic cell to tetragonal. Thirdly, the V–D distance in this form must be shorter than that in γ V_4D_3. The only possible site which satisfies the above three conditions is the octahedral site (o-site), whose EFG is symmetric with respect to the c axis.

Next, let us determine the ordered deuterium arrangement in β V_2D. Consider that there are n deuterium atoms and $6n$ o-sites in a ordered V_2D unit cell. However, it is necessary to consider only $2n$ o-sites because of their symmetry with respect to the c axis. Thus, the problem can be reduced to a manner of selecting n o-sites from $2n$ o-sites.

Consider a linear array of vanadium atoms with a spacing of c_0 along the c axis. The o-sites are at the middle of the V–V axis, standing in a line with the same spacing of vanadium:

-V-O-V-O-V-O-V-O-V-O-V-O-V-O-V-

If a deuterium atom occupies an o-site, it would displace the two nearest-neighboring vanadium atoms by $\pm z$. Consequently, it becames geometrically difficult for deuterium to occupy the two nearest-neighboring o-sites and the array of deuterium atoms will be:

-V-D-V-E-V-D-V-E-V-D-V-E-V-D-V-E-V-

where E means that the site is empty. A translation of the above one-dimensional lattice points by $\pm 1/2$ $1/2$ $1/2$ determine the array of atoms on the next side. Thus, we obtain a three-dimensional arrangement of deuterium, as is shown in Fig. 1. This structure is

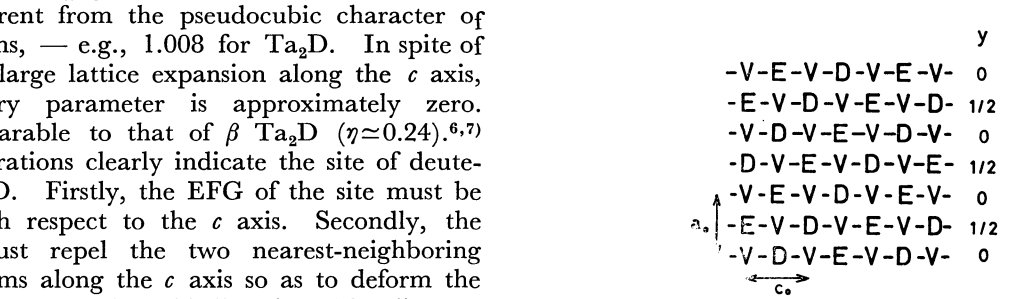

Fig. 1. Three-dimensional arrangement of β V_2D, a projection onto (010) plane.

consistent with the results of a recent neutron diffraction study[8] except for the existence of a small proportion of tetrahedral occupation in that study.

It should be noted that there are $4n$ tetrahedral sites (t-sites) whose EFG is symmetric with respect to the c axis. Therefore, the occupation of these t-sites by deuterium may not be negligible. However, at high temperatures, this effect does not change the principal axis directions and the asymmetry parameter of the EFG, but changes only the principal value of the EFG.

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Table 1.

$K\times10^{-8}$ cm	$\lvert(eq)_{tet}\rvert/\lvert(eq)_{oct}\rvert$
1.8	0.412
1.5	0.449
1.0	0.511

Thus, from the temperature dependence of the deuteron quadrupole coupling constant, we can, in principle, determine the proportion of the *t*-occupation of the deuterium. It has been shown that about 5% of deuterium atoms are in the *t*-sites.[8] Since the sign of the EFG of the *t*-site is the reverse that of the *o*-site, the following simple relation may be hold:

$$[(e^2qQ/h)^{\beta}_{oct}\times0.95]-[(e^2qQ/h)^{\beta}_{tet}\times0.05]=(e^2qQ/h)_{\beta}=68.6\text{ KHz (R.T.)}$$

where $(e^2qQ/h)^{\beta}_{oct}$ and $(e^2qQ/h)^{\beta}_{oct}$ are the quadrupole coupling constants for the *o*- and *t*-sites of the tetragonal β V_2D respectively. With the $(e^2qQ/h)^{\beta}_{tet}\simeq(e^2qQ/h)_{\gamma}=37.5$ KHz approximation, $(e^2qQ/h)^{\beta}_{tet}$ is calculated to be 74.2 KHz, larger by about 10.8% than the observed value.

It is of interest to compare the experimental quadrupole coupling constant ratio $(e^2qQ/h)_{\gamma}/(e^2qQ/h)^{\beta}_{oct}\simeq0.5$ with that calculated from the simple electrostatic model used in the previous paper.[7] With a_0 3.00 Å and c_0 3.1 Å for β V_2D (*o*-site) and with $a_0=3.16$ Å for γ V_4D_3 (*t*-site), the calculated ratio for three values of the screening constant is shown in Table 1. A comparison of the values in the table with the experimental one shows that $K=1.1\times10^8$ cm^{-1} is suitable in this case. However, it has elsewhere been shown[7] that a value of $K=1.8\times10^8$ cm^{-1} is most suitable for the Ta-D system if the charge on the Ta ion is 5. Thus, the discrepancy in the K value seems to indicate the limit of the application of the electrostatic model to the high-concentration interstitial systems.

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