NQR and Low-Field NMR of ^{181}Ta in the Low-Temperature CDW State of $2H\text{-}TaS_2$

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NQR and low-field NMR spectra of ^{181}Ta are reported to probe the electronic environment of inequivalent tantalum sites in the low-temperature CDW state of a layered compound $2H\text{-}TaS_2$. The overall features are found to be consistent with the structure consisting of nine-atom snowflake clusters in a locally commensurate CDW state.

Key words: NQR, NMR, ^{181}Ta, CDW, TaS_2.

Transition metal dichalcogenides have been the subject of intensive research because of their electronic instabilities which result in charge density waves (CDW) [1]. The 2H-polytype of TaS_2 undergoes a phase transition at 75 K from the high-temperature normal metallic state to the incommensurate CDW state with wave vector of 0.338 a_0* [2]. We report here the result of a pulsed NQR study of ^{181}Ta together with a reinvestigated spectrum of low-field NMR of ^{181}Ta in the low-temperature phase of $2H\text{-}TaS_2$ at 4.2 K.

The quadrupole moment of ^{181}Ta ($I = 7/2$) is very large ($Q = 3.28$ barn), and NQR of ^{181}Ta was found to be useful for the study of the local electronic environments around Ta nuclei, as was demonstrated in a case of $1T\text{-}TaS_2$ [3]. A pulsed NQR spectrum of ^{181}Ta in $2H\text{-}TaS_2$ at 4.2 K was taken using an incoherent high-power rf oscillator and a highly sensitive receiving system. A somewhat complex NQR spectrum of ^{181}Ta has been obtained at 4.2 K as shown in Fig. 1, with clear peaks at frequencies of 95.5, 140, 190.2, 194.0 MHz and weak ones at 105.3 and 284.6 MHz. The peak positions of the spectrum are reliable but relative intensities should be considered to be only qualitative. A single Ta site creates three NQR transitions of $\pm 1/2 \leftrightarrow \pm 3/2$, $\pm 3/2 \leftrightarrow \pm 5/2$ and $\pm 5/2 \leftrightarrow \pm 7/2$, and the ratios of the three frequencies are determined by the asymmetry parameter η as

$$\eta = (V_{xx} - V_{yy})/V_{zz}, \tag{1}$$

where V_{zz}, V_{yy}, and V_{zz} are the principal values of electric field gradient (EFG) tensor at the resonant nuclei, and $|V_{zz}| \geqq |V_{yy}| \geqq |V_{xx}|$.

If the assignment for the three transitions is done, the quadrupole frequency

$$\nu_Q = 3\,e^2 q Q/[2I\,(2I-1)\,h] \tag{2}$$

can be determined. The peak frequencies of 95.5, 190.2 and 284.6 are in the ratio of nearly 1:2:3, indicating the existence of a Ta site with nearly axial symmetry ($\eta = 0.03$). But the assignment of the other peaks in Fig. 1 to the NQR transitions is not unique due to possibilities that some transitions are overlapping and that some transitions (probably $\pm 5/2 \leftrightarrow \pm 7/2$) are missing. Therefore, we analyze our data with the help of low-field NMR and TDPAC experiments, as is described below.

The powder spectra of ^{181}Ta NMR in a swept magnetic field for the transitions between degenerate NQR states $\pm m$ have shown to be a good method to give values of η of the EFG independent of the magnitude of the EFG (or the magnitude of the quadrupole frequency) if the NMR frequency is much smaller than ν_Q [4]. The signals from the $\pm 1/2$ transitions are ex-

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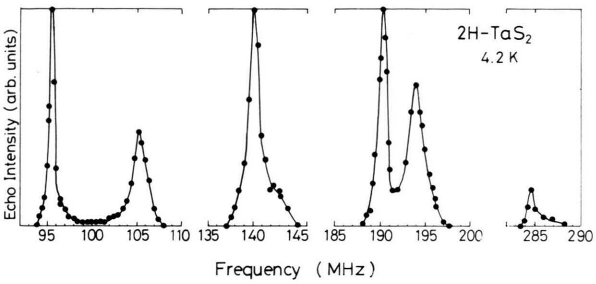

Fig. 1. NQR spectrum of ^{181}Ta in 2H-TaS_2 at 4.2 K.

Table 1. Assignment of the peak frequencies (MHz) in Fig. 1 to the NQR transitions and derived values of η and ν_Q for the three Ta sites in 2H-TaS_2 at 4.2 K.

Ta site	*A*	*B*	*C*
f ($\pm 1/2 \leftrightarrow \pm 3/2$)	105.3	105.3	95.5
f ($\pm 3/2 \leftrightarrow \pm 5/2$)	140.0	194.0	190.2
f ($\pm 5/2 \leftrightarrow \pm 7/2$)	(221) *	(293) *	284.6
η	0.37 ± 0.02	0.15 ± 0.02	0.03 ± 0.03
ν_Q (MHz)	75.2 ± 0.5	98.4 ± 0.5	95.5 ± 0.2

* Signals at frequencies with parentheses were not observed.

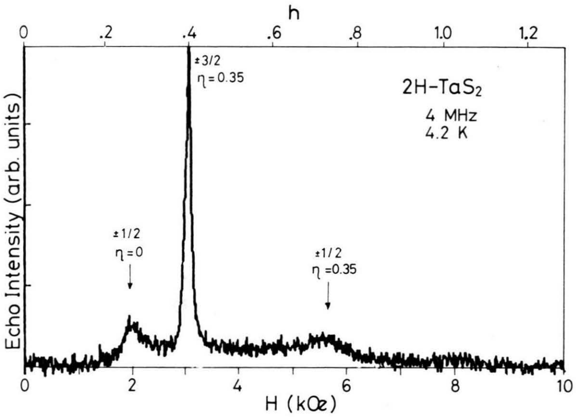

Fig. 2. A powder spectrum of low-field NMR of 181Ta in 2H-TaS_2 at 4.2 K at a frequency of 4 MHz. $h = H/H_0$, where H_0 is the resonance field for a free ^{181}Ta. Assignments of transitions are shown.

pected to be strong if $\eta \leqq 0.2$, and the signals from the $\pm 3/2$ transitions are expected to be strong if $\eta \geqq 0.15$. Particularly, if the value of η is 0.35, the case which is called magic asymmetry, the width for the $\pm 3/2$ transition vanishes in a first order calculation and the signal becomes quite strong. The $\pm 5/2$ and $\pm 7/2$ transitions are not expected to be observable because of the extremely large widths. The shape of a powder spectrum depends strongly on η and η can be determined easily if the Ta site has a special value of η [4, 5]. The low-field NMR of ^{181}Ta in 2H-TaS_2 has been reinvestigated and a spectrum recorded at 4.2 K and 4 MHz is shown in Figure 2. The $\pm 1/2$ transition for $\eta = 0$ and $\eta = 0.35$, and the $\pm 3/2$ transition for $\eta = 0.35$ are clearly seen. This indicates that there exist at least two distinct Ta sites with η nearly 0 and 0.35. The number of inequivalent Ta sites can be more than two, because Ta sites with nearly the same values of η give nearly the same NMR spectrum even if the values of ν_Q are quite different. Experiments at 17 MHz have also been done, but no appreciable frequency (or field) dependence was observed *.

Experiments of TDPAC have already been done on 2H-TaS_2 [6, 7], and we can use those results for the present analysis. The Fourier-transformed TDPAC spectrum shows three sites with equal population with η's of 0.00, 0.10 and 0.36 [6] (or refined values of 0.10, 0.11 and 0.37 [7]). The existence of three sites was discussed using the nine-atom snowflake cluster model in which the charge-density extrema are at the center of a triangle formed by three Ta atoms (A site) and B and C sites are peripheral atoms. The present data of NQR and NMR are consistent with the TDPAC data and all peaks in Fig. 1 except the signals from the Ta site with $\eta = 0.03$ are assigned using the TDPAC data with the obtained parameters shown in Table 1. In particular, the possibility that the peaks at 140.0 and 194.0 MHz are due to $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ transitions from a Ta site with $\eta = 0.35$, respectively, is excluded from the TDPAC experiments, although the frequency ratio is 1.39, which is expected for $\eta = 0.35$. It is to be noted that the fine structures were observed in NQR spectra of 1T-polytypes and interpreted as arising from the stacking order of CDW's [3], but they were not seen in the case of 2H-TaS_2.

In summary, the overall features of the NQR and low-field NMR spectra are consistent with the nine-atom snowflake cluster model proposed from the TDPAC experiments. Three inequivalent Ta sites have definite values of the quadrupole parameters in spite of the incommensurate CDW state observed by dif-

* The NMR spectrum in 2H-TaS_2 in Fig. 2 is different from Fig. 4 in the first report [4] as was suggested in [5]. The sample in the first report was probably 4H_b-TaS_2; the detail will be reported elsewhere.

fraction experiments. The signals must come from locally commensurate regions separated by regions of phase slip, confirming again the concept of discommensurations.

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