NMR study on a 2H-NbSe$_2$ single crystal: A microscopic investigation of the charge density waves state†

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Abstract. We present a pulsed NMR study on a single crystal of 2H-NbSe$_2$ at atmospheric pressure and under hydrostatic pressure of 21 kbar in the temperature range 4.2-273 K. Analysis of Knight shift (KS) and nuclear spin–lattice relaxation (NSLR) time data in the normal state are consistent with $N(E_F) = 2.4$ states/eV spin and an admixture of 40% of $d_{x^2}$ and $d_{x^2-y^2}$ wavefunctions in the $d_{x^2}$ band. The product $T_1 T = 500 \pm 100$ ms K was found constant in the temperature range 4.2-77 K and pressure independent; measurements at the ‘magic angle’ indicate an orbital contribution $(T_1 T)^{-1} \approx 0.9 \pm 0.9$ (s K)$^{-1}$. The pressure dependence of KS and the electric field gradient tensor (EFG) were respectively found to be:

$$\frac{\partial \ln K}{\partial \ln V} = 5 \pm 1 \quad \text{and} \quad \frac{\partial \ln q}{\partial \ln V} = 3 \pm 0.5.$$

Our results are consistent with the onset of incommensurate charge density waves (ICDw) at $T_0 = 33$ K at $P = 1$ bar and $T_0 = 26$ K at 21 kbar. Below $T_0$, the lineshapes of the $m \rightarrow m+1$ transitions agree with a local distribution of KS and EFG respecting the symmetry of a triple ICDW with a maximum value of 9% for the redistribution of conduction electrons within an atomic cell. Above $T_0$, nuclear spin–spin relaxation measurements demonstrate that the observed pretransitional broadening of the lines is due to static CDW fluctuations, induced by impurities.

1. Introduction

The transition metal dichalcogenide layer compounds have been the subject of intense experimental work since the discovery that many of them undergo periodic lattice distortion (PLD) accompanied by charge density waves (CDW) (Wilson et al 1975). The origin of this structural phase transition is due to the cylindrical nature of this Fermi surface, favouring good ‘nesting’ (Chan and Heine 1973) or to the possible existence of Van Hove singularities in the band structure close to the Fermi level (Rice and Scott 1975). In the trigonal prismatic polytypes of the 5d$^1$ transition metal dichalcogenides, the phase transition between the normal metallic state and the incommensurate PLD/CDW state is accompanied by a weak resistance anomaly (Harper et al 1975) and in most of them the structural phase transition does not prevent the occurrence of superconductivity at lower temperatures.

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temperature. Experiments at high hydrostatic pressure have demonstrated that the presence of a CDW in the crystal lowers the superconducting temperature $T_c$ and that the suppression of the structural instability under high pressure could restore a higher value of $T_c$ (Berthier et al. 1976a, b, c, Jerome et al. 1976). This was interpreted as an effect of the density of states (Friedel 1975) and a search of this variation of $N(E_F)$ at the onset of the PLD/CDW was one of the motives for undertaking an NMR study in 2H-NbSe$_2$. This compound, in which $T_0 = 33.5$ K (Moncton et al. 1975) and $T_c \approx 7.2$ K has been the subject of several NMR studies in the last few years (Ehrenfreund et al. 1971, Valic et al. 1974, Berthier et al. 1976a, b, Wada 1976, Torgeson and Borsa 1976, Borsa et al. 1977, Stiles and Williams 1976) due to the good sensitivity of the $^{93}$Nb nucleus.

In this paper, we present a pulsed NMR study on the $^{93}$Nb nuclei in a single crystal of 2H-NbSe$_2$ at ambient pressure and under hydrostatic pressure of 21 kbar in the temperature range 4.2–273 K. This includes Knight shift (KS), electric field gradients (EFG), lineshapes nuclear spin–lattice and spin–spin relaxation time measurements.

Part of the results have already been presented in a preceding paper (Berthier et al. 1976b, referred to as BJMR); we shall re-examine the results in the light of the new experiments along the following lines: In §2, we shall discuss the experimental technique and sample preparation. The experimental results will be presented in §3, and will be discussed in §4 in the following manner: In §4.1 we shall discuss nuclear spin–lattice relaxation (NSLR) and Knight shift (KS) measurements with respect to the electronic band structure of the compound, as well as the pressure dependence of KS and EFG. In §4.2, we shall discuss properties of the lineshape of the different transitions between Zeeman levels in connection with the onset of the CDW. We shall finally discuss in §4.3 the effect of fluctuations of the CDW on the lineshape and the relaxation of $^{93}$Nb.

2. Experimental technique

All measurements were performed by using pulsed NMR techniques in a single crystal of 2H-NbSe$_2$. The sample was grown by vapour transport at 780°C using iodine as the transport agent. The polytype was confirmed by x-rays. The value of $T_c = 7.1$ K (Garoche et al. 1976) measured in samples of the same batch indicates good stoichiometry and the resistivity ratio $\rho(273)/\rho(10) \approx 60$ equals the best values quoted in the literature (Huntley and Frindt 1974). The weight of the crystal was 98 mg. The temperature was measured with a gold iron/chromel thermocouple with reference in helium bath. Experiments at hydrostatic pressure of 21 kbar were performed in a teflon cell using a mixture of isopentane and amyl alcohol as pressure transmitter. The whole pressure apparatus has been described elsewhere (Delaplace et al. 1976).

The measurement frequency was 28 MHz, and in some cases 15 MHz. Lineshape and KS measurements were performed by Fourier transform of free induction decay or spin-echo using a boxcar averager. $T_1$ measurements in the orientation $H_0 \parallel c$ axis were achieved by measuring the recovery of the magnetisation of the $(1/2 \rightarrow -1/2)$ transition after a comb of saturation RF pulses. In the case of measurements at the ‘magic angle’ an attempt was made by modulation of the RF frequency during the comb to saturate all the $(m \rightarrow m - 1)$ transitions. Spin–spin relaxation time measurements on the $(1/2 \rightarrow -1/2)$ transition ($H_0 \parallel c$ axis) were achieved by recording the whole line to avoid disturbance due to ringing after the RF pulses.
3. Experimental results

The $^{93}$Nb nucleus has an $I = 9/2$ spin and a quadrupole moment $Q = 0.16 \times 10^{-24}$ cm$^2$. Assuming that the EFG at the Nb site possesses axial symmetry, which is true at least in the absence of a CDW, the spin can be described by the following Hamiltonian (Abragam 1961):

$$ \mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_{\text{dip}} $$

where

$$ \mathcal{H}_Z = -\sum_i \gamma_i H_0 [1 + K_{\text{iso}}(R_i) + K_{ax}(R_i)(3\cos^2 \theta_i - 1)] I_z $$

$$ H_Q = \sum_i \frac{1}{2} h \omega_Q(R_i) \left\{ \frac{1}{2} (3\cos^2 \theta_i - 1)(I_z^2 - \frac{1}{3} I(I+1)) + \frac{1}{2} \sin \theta_i \cos \theta_i \right\} $$

$$ \times (I_z^2 I_{z+}^2 + I_{z+}^2 I_{z+}^2 + \cdots) + \frac{1}{2} \sin^2 \theta_i [I_{z+}^2 + I_{z-}^2] \right\} $$

$\mathcal{H}_{\text{dip}}$ is the usual dipole–dipole Hamiltonian and $h \omega_Q(R_i) = 3 e^2 q Q(R_i)/2(2 I - 1)$, where $e \rho_q(R_i) = V_{zz}(R_i)$ is the main component of the electric field gradient tensor at site $R_i$, which is along the c-axis of the crystal; $\theta_i$ is the angle between the magnetic field $H_0$ and the c-axis of the crystal.

Most of the experiments were performed for the particular orientation $H_0 || c$ axis. In this case, the resonance frequencies of a nucleus at site $R_i$ are given by:

$$ h \omega_{m \rightarrow m-1}(R_i) = -\gamma_i H_0 [1 + K_{||}(R_i)] + h \omega_Q(R_i)(m - \frac{1}{2}) $$

In the absence of a CDW, $K_{||}(R) = K_{\text{iso}} + 2K_{ax}$ and $\omega_Q(R)$ are independent of $R$ and the spectrum consists of nine lines with a dipolar width of about 10 G. Values of $K_{||}$ and $\omega_Q$ for different values of $T$ and $P$ in the normal phase are given in table 1.

| Table 1. Knight shifts and electric field gradient at various temperature and pressure in $2H-NbSe_2$. |
|-----------------|-----------------|-----------------|
| $P = 1$ bar     | $P = 21$ kbar   |
|-----------------|-----------------|-----------------|
| $T$(K)          | $K_{||}$ (%)     | $e^2 q Q/h$(MHz)| $T$(K)          | $K_{||}$ (%)     | $e^2 q Q/h$(MHz)|
| 273             | 0.42 ± 0.02     | 60.12 ± 0.2     | 127            | 0.30 ± 0.02     | 60.50 ± 0.2     |
| 77              | 0.38 ± 0.02     | 61.98 ± 0.2     | 77             | 0.30 ± 0.02     | 60.77 ± 0.2     |
| 50              | 0.37 ± 0.02     | 62.13 ± 0.2     | 30             | 0.30 ± 0.02     | 60.96 ± 0.2     |

The temperature dependence of the lineshape of the $(-\frac{1}{2} \rightarrow -\frac{3}{2})$ transition at ambient pressure is represented in figure 1. At room temperature, the linewidth is purely dipolar and equal to 8.5 ± 1 G. It starts to increase already at liquid nitrogen temperature down to the onset temperature of the PLD, $T_0 = 33$ K. This linewidth variation is plotted in figure 2. Below $T_0$, there is a sudden increase of the linewidth with the appearance of a structure in the line. The total width at 4.2 K is 300 G. As will be seen later, this is due to a spatial modulation of the amplitude of the EFG due to the onset of a triple incommensurate CDW.

The temperature dependence of the linewidth of the $(\frac{1}{2} \rightarrow -\frac{1}{2})$ transition is plotted in figure 3. It is constant and equal to 12 ± 1 G down to 33 K and then the line suddenly broadens. This broadening corresponds to the appearance of a structure similar to that observed in the $(-\frac{1}{2} \rightarrow -\frac{3}{2})$ transition (figure 4); measurements at 28 MHz and 15 MHz
Figure 1. Evolution of the \((-\frac{1}{2}, -\frac{1}{2})\) transition as a function of temperature \((P = 1\) bar). The solid line represents the calculated lineshape for an EFG distribution associated with a triple incommensurate CDW.

Figure 2. Temperature dependence of the linewidth of the \((-\frac{1}{2}, -\frac{1}{2})\) transition above \(T_0\).
**Figure 3.** Linewidth of the central line \((\frac{1}{2}, -\frac{1}{2})\) as a function of temperature \((P = 1 \text{ bar})\).

**Figure 4.** Lineshape of the central line \((\frac{1}{2}, -\frac{1}{2})\) below 33 K \((P = 1 \text{ bar})\). The solid line is the calculated lineshape corresponding to a Knight shift distribution associated with a triple CDW.

show that the extent of that structure is proportional to \(H_0\), so that it corresponds to a Knight shift distribution and not to second-order quadrupolar broadening. A detailed study of the temperature dependence of the linewidth close to the transition temperature was not possible because of the slight inhomogeneous quadrupole broadening of the line due to crystal imperfections, which was temperature independent. As the \((-\frac{1}{2} \rightarrow -\frac{3}{2})\) transition, observed in higher field than the \((\frac{1}{2} \rightarrow -\frac{1}{2})\) transition, was narrower than this latter we can say that these imperfections mainly cause a distribution of \(\theta\) around the value \(\theta = 0\), rather than a distribution of the amplitude of \(v_0\), which would cause a first-order quadrupole broadening of the \(m \rightarrow m - 1\) transitions \((m \neq \frac{1}{2})\).
The temperature dependence of the lineshape of the \((-\frac{1}{2} \rightarrow -\frac{3}{2})\) transition at 21 kbar is shown in figure 5. Again a pretransitional broadening is observed and we deduced an onset temperature for the CDW of \(T_0 = 26\) K which corresponds to the appearance of a structure in the line. The total extent of the structure at 10 K is about 230 G. No structure was resolved on the \((\frac{4}{2} \rightarrow -\frac{1}{2})\) line. This is not surprising since inhomogeneous quadrupolar broadening was more severe, due to supplementary strains induced in the sample, and the extent of the structure is expected to be smaller, as it is for the \((-\frac{1}{2} \rightarrow -\frac{3}{2})\) transition.

3.1. Relaxation time measurements

In the orientation \(H_0||e\)-axis, NSLR time \(T_1\) was measured at the frequency of 28 MHz recording the recovery of the magnetisation of the \((\frac{1}{2} \rightarrow -\frac{3}{2})\) transition at times \(t\) after a comb of saturating RF pulses. In figure 6 we have plotted \(|(M(\infty) - M(\tau))/M(\infty)|\) for various temperatures \(T\) in the range 4.2–273 K in a reduced time scale where \(\tau = t T/273\). The results show that \(T_1 T\) remains constant within the error bars at least between 4.2 and 77 K. As far as \(T_1\) values are concerned, one must remember that we saturate only the \((\frac{1}{2} \rightarrow -\frac{3}{2})\) transition, the others being at least 2.5 MHz apart. In such a case, assuming a unique relaxation mechanism depending only on \(|\langle m|I_m|m + 1\rangle|^2\) one expects the following behaviour for \(M(t)\) (Andrew and Tunstall 1961 Simmons et al 1962, Narath 1967).

\[
|M(\infty) - M(t)|/M(\infty) = 0.65 e^{-90Wt} - 0.22 e^{-56Wt} - 0.09 e^{-30Wt} - 0.03 e^{-12Wt} - 0.006 e^{-2Wt}
\]

(2)

where \(2W = (T_1)^{-1}\). The best fit of our data with formula (2) leads to \(T_1 T = 500 \pm 100\) ms K in the range 4.2–77 K. (Assuming complete or partial (60\%) saturation give results close to
XMR study on a $2\text{H-NbSe}_2$ single crystal

Figure 6. Recovery of the magnetisation of the $(\frac{1}{2}, -\frac{1}{2})$ transition as a function $\tau = \Delta t T/273$. Here $\Delta t$ is the time interval between a comb of saturating RF pulses and the lecture pulse. The solid lines are the theoretical expression for $[M(\infty) - M(t)]/M(\infty)$ according to equation (2) for $T_i T = 545, 500$ and $475 \text{ ms K}$. These disagree with the value reported by Wada (1976) which we think to be due to a misinterpretation of experimental data. The same measurements were performed under hydrostatic pressure of $21 \text{ kbar}$, in the temperature range $10-110 \text{ K}$. Within the error bars we found the same value of $T_i T$.

In order to confirm the $T_i T$ deduced by fitting of the data in the orientation $H_0 \parallel c$ axis, we performed a few measurements of NSLR time at ambient pressure, with the crystal oriented at $\theta = 56^\circ$ and $\theta = 0^\circ$.

Figure 7. Recovery of the magnetisation for two different temperatures, for $\theta = 0^\circ$ and $\theta = 56^\circ$. The difference between the two orientations is not due to anisotropy of $T_i$ but to different initial conditions (see the text).
the magic angle \((3 \cos^2 \theta - 1 = 0)\). In these conditions, the overall extent of the NMR spectrum of \(^{93}\text{Nb}\) is reduced to about 1 kG, and we can hope to saturate all the \(m \rightarrow m - 1\) transitions which would lead to single exponential behaviour for \(|M(\infty) - M(t)|/M(\infty)\) with a time constant \(T_1\). In figure 7, one can see the different behaviour of \(|M(\infty) - M(t)|/M(\infty)\) for \(\theta = 0\) and \(\theta = 56^\circ\). For this last orientation, we did not succeed in achieving a complete saturation, but an important part of the magnetisation recovers with the time constant \(T_1 = (2W)^{-1}\). In table 2 we give the values of \(T_1\) and \(T_1 T\) for a few temperatures above \(T_0\).

### Table 2.

<table>
<thead>
<tr>
<th>(T (K))</th>
<th>(T_1 (\text{ms}))</th>
<th>(T_1 T (\text{ms K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>7.4 ± 1.8</td>
<td>244 ± 60</td>
</tr>
<tr>
<td>51</td>
<td>6.3 ± 2</td>
<td>320 ± 100</td>
</tr>
<tr>
<td>71</td>
<td>4.7 ± 0.9</td>
<td>334 ± 65</td>
</tr>
<tr>
<td>114</td>
<td>3.7 ± 0.7</td>
<td>427 ± 85</td>
</tr>
</tbody>
</table>

We also measured the spin–spin relaxation time \(T_2\) at 51 K and found \(T_2 = 240 ± 60 \mu s\), whereas the linewidth is equal to about 30 G.

### 4. Discussion

#### 4.1 Analysis of KS and NSLR data with respect to the electronic band structure

According to the hexagonal symmetry of the Nb sites in the crystal, the Knight shift in the normal state can be written:

\[
K = K_{\text{iso}} + K_{\text{ax}}(3 \cos^2 \theta - 1).
\]

The different contributions to \(K_{\text{iso}}\) are respectively the contact term with s electrons, the core polarisation \(K_{\text{sp}}\), and the orbital term \(K_{\text{orb}}\). According to the band structure calculations of Matheiss (1973), the conduction band has purely d character and the s–p bands are repelled well below or well above the Fermi level. We shall therefore neglect \(K_{\text{ax}}\) in the following discussion. The contributions to \(K_{\text{ax}}\) are respectively from orbital \((K_{\text{orb}}^o)\) and dipolar \((K_{\text{orb}}^d)\) origin.

By plotting \(K_{\text{int}}(T)\) against the susceptibility measured on powder, \(\chi(T)\), one can determine the core polarisation hyperfine field \(H_{\text{sp}}\) (Clogston et al 1964). Using the susceptibility measurements of Marezio et al (1972), and combining the Knight shift data of Valic et al (1974) and ours, we deduce:

\[
H_{\text{sp}} = (0.11 ± 0.07) \times 10^6 \text{ Oe per Bohr magneton}.
\]

The large uncertainty of this value is due to the small variation of both \(K\) and \(\chi\) in the temperature range studied. We note that the atomic value, which is usually taken without any correction for metals is \(0.21 \times 10^6 \text{ Oe}/\mu_\text{B} \) (Yafet and Jaccarino 1964). But we are here dealing with a covalent compound, and one expects the valence s–p wavefunctions of the transition ion to be strongly hybridised with the s–p wavefunctions of the selenium, which can strongly affect the final value of \(H_{\text{sp}}\).

Let us now consider the NSLR data; according to Matheiss (1973), the wavefunctions of the conduction band electrons are essentially of \(d_{z^2}\) symmetry, but strongly hybridised with \(d_{xy}\) and \(d_{x^2-y^2}\) wavefunctions. We shall call \(c\) and \(1 - c\) the respective amount of \(d_{z^2}\) and \(d_{xy}\).
The relaxation rate can be written (Narath 1967)

\[ (T_1 T)_{\text{cp}}^{-1} = (4\pi k_B/\hbar)(\gamma_n h H_{\text{eff}}^2)[N_d(E_F)]^2[c^2 + \frac{1}{2}(1 - c)^2] \]  

\[ (T_1 T)_{\text{orb}}^{-1} = (4\pi k_B/\hbar)(\gamma_n h H_{\text{orb}}^2)[N_d(E_F)]^2(1 - c)^2 \sin^2 \theta. \]  

We shall neglect the dipolar contribution for which the symmetry reduction factor is much more severe.

For \( \theta = 0 (H_0 || e \text{ axis}) \), the relaxation rate is due only to core polarisation mechanism. Using the Korringa relation, where we neglect the electron-electron interaction.

\[ K^2 \Gamma(c) = (h/4\pi k_B)(T_1 T)_{\text{cp}}^{-1} (\gamma_n/\gamma_e)^2 \]

where \( \Gamma(c) = c^2 + \frac{1}{2}(1 - c)^2 \), we obtain \( K_{\text{cp}} \Gamma(c)^{1/2} = (0.295 \pm 0.03) \times 10^{-2} \), that is \( -0.51 \% \leq K_{\text{cp}} \leq -0.29 \% \). From the NSLR rate measured at the magic angle \( T_1 T = (370 \pm 80) \text{ ms} \ K \) we deduce \( (T_1 T)^{-1} \text{total} - (T_1 T)^{-1} = 0.9 \pm 0.9 \text{ sK}^{-1} \).

Taking \( N_d(E_F) = 3\gamma_n/2\pi^2 k_B^2(1 + \lambda) \sim 2.4 \text{ states per eV atomic spin from specific heat and superconducting measurements of Garoche et al (1976) and } H_{\text{ef}}^\text{orb} = 0.285 \times 10^6 \text{ Oe (Yafet and Jaccarino 1974) we get from equation (4)} \)

\[ c = 0.37 \pm 0.06. \]

From the corresponding value of \( \Gamma(c) \), we finally conclude that \( K_{\text{cp}} = 0.46 \pm 0.05 \% \) and that the admixture of \( d_{xy} \) and \( d_{x^2-y^2} \) wavefunctions at the Fermi level is of the order of 37 \%.

This leads to \( H_{\text{ef}}^\text{orb} = 0.17 \times 10^6 \text{ Oe} \), in agreement with the \( K \) versus \( \chi \) analysis, and \( \chi_{\text{spin}}^\text{ax} = 2N\mu_B^2 N_d(E_F) = 155 \times 10^{-6} \text{ emu mol}^{-1} \).

Now from the usual \( K(T) \) versus \( \chi(T) \) analysis (Clogston et al 1964) taking \( H_{\text{ef}}^\text{ax} = -0.17 \times 10^6 \text{ Oe}, H_{\text{ef}}^\text{orb} = 0.285 \times 10^6 \text{ Oe} \), the diamagnetic contribution of Se equal to \( -42 \text{ emu mol}^{-1} \) (deduced from susceptibility of pure Se (Lasjaunias 1973) and \( K_{\text{iso}}(77) = 0.00 \pm 0.02 \% \) (Valic et al 1974), one gets:

\[ K_{\text{cp}}^{\text{iso}} = -0.46 \% \quad \chi_{\text{spin}}^\text{ax} = 155 \text{ emu mol}^{-1} \]

\[ K_{\text{orb}}^{\text{iso}} = +0.46 \% \quad \chi_{\text{orb}} = 85 \text{ emu mol}^{-1}. \]

Let us now consider the axial part of the Knight shift tensor, which has two contributions:

(a) The orbital one, usually expressed as (Jaccarino 1967)

\[ K_{\text{orb}} = \sum_{k,n,n'} \frac{\langle k,n|L|k,n'\rangle}{E_{k,n} - E_{k,n'}} \]

may be decomposed into two terms:

(i) a contribution from states within the two \( d_{z^2} \) bands; matrix elements presumably are small, but \( E_{k,n} - E_{k,n'} \) are small too (\( \sim 0.5 \text{ eV} \)). As the wavefunctions have symmetry restricted to \( l_z = 0 \) or \( l_z = \pm 2 \), one has \( K_{\text{iso}} = K_{\text{xx}} \) for this contribution.

(ii) a contribution from states of the \( d_{z^2} \) bands and the upper d-bands. The order of magnitude for \( K_{\text{orb}} \) is given by (Jaccarino 1967).

\[ K_{\text{orb}}^\text{ax} = 2N\Omega \frac{n_u n_0}{n_u + n_0} \frac{\beta^2}{\Delta E} \langle r^{-3} \rangle \sim 3 \times 10^{-2} \]

where \( n_0 \) the number of electrons = 1, \( n_u \) the number of holes in the upper d-bands = 8; \( \Delta E \) was chosen equal to 3 eV from the calculations of Matheiss and \( N\Omega = 39 \text{ cm}^3 \) is the molar
volume. Although this estimation clearly overestimates the real value of \( K_{\text{orb}} \), it shows that this contribution cannot be neglected.

(b) The dipolar one which may be expressed in the tight-binding approximation as

\[
K_{\text{dip}}^\text{ex} = \langle 1 - 3 \cos^2 \theta \rangle \frac{1}{r^3} \frac{\chi_{\text{d}}^\text{spin}}{2N}
\]

where \( \theta \) is the angle between \( r \) and the \( c \) axis of the crystal.

For a pure \( d_{z^2} \) band, this gives:

\[
K_{\text{dip}}^\text{ex} = \frac{2}{3} \langle r^{-3} \rangle \chi_{\text{d}}^\text{spin} / 2N \simeq 0.05 \times 10^{-2}.
\]

We finally resume this analysis in table 3 where we give the various contributions to the \( K_S \), the susceptibility, the values of hyperfine fields, the different contributions to the relaxation and the percentage of admixture of \( d_{xy} \) and \( d_{x^2-y^2} \) wavefunctions in the \( d_{z^2} \) band at the Fermi level.

Table 3.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Value (emu mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{exp}} ) at 77 K</td>
<td>-0.46 ± 0.05</td>
</tr>
<tr>
<td>( K_{\text{orb}} ) (%)</td>
<td>0.46 ± 0.07</td>
</tr>
<tr>
<td>( K_{\text{dip}} ) (%)</td>
<td>0</td>
</tr>
<tr>
<td>( K_{\text{dip}}^\text{ex} )</td>
<td>0.14</td>
</tr>
<tr>
<td>( K_{\text{dip}}^\text{ex} )</td>
<td>0.05</td>
</tr>
<tr>
<td>( K_{\text{orb}} ) (Valic et al 1974)</td>
<td>2 ± 0.4</td>
</tr>
<tr>
<td>( (T_1 T_{\text{exp}}^{-1} s^{-1} K^{-1}) ) at 56 K</td>
<td>0.9 ± 0.9</td>
</tr>
<tr>
<td>( H_{\text{rf}} ) (Oe/( \mu_B ))</td>
<td>0.17 ± 0.01 \times 10^6</td>
</tr>
<tr>
<td>( H_{\text{orb}} ) (Oe) (Yafet and Jaccarino 1964)</td>
<td>0.285 \times 10^6</td>
</tr>
<tr>
<td>( 1 - C %d_{xy} ) and ( d_{x^2-y^2} ) at Fermi level</td>
<td>0.37 ± 0.07</td>
</tr>
<tr>
<td>( \chi_{\text{d}}^\text{spin} ) (emu mol(^{-1})) at 77 K</td>
<td>155</td>
</tr>
<tr>
<td>( Z_{\text{orb}} ) (emu mol(^{-1}))</td>
<td>85</td>
</tr>
<tr>
<td>( Z_{\text{dis}} ) (emu mol(^{-1}))</td>
<td>-42</td>
</tr>
<tr>
<td>( N_d(E_F) ) (states per eV atomic spin)</td>
<td>2.4 ± 0.2</td>
</tr>
</tbody>
</table>

We now discuss the pressure dependence of the Knight shift. Taking the compressibility data of Jones et al (1972), one obtains \( \partial \ln K / \partial \ln V \simeq 5 \) at room temperature. As we neglect any \( s \) contribution to the Knight shift, one has:

\[
\frac{\partial \ln K}{\partial \ln V} = \frac{K_{\text{dp}}}{K} \frac{\partial \ln K_{\text{dp}}}{\partial \ln V} + \frac{K_{\text{orb}}}{K} \frac{\partial \ln K_{\text{orb}}}{\partial \ln V} = -1.1 \frac{\partial \ln K_{\text{dp}}}{\partial \ln V} + 2 \frac{\partial \ln K_{\text{orb}}}{\partial \ln V}.
\]

From \( T_1 \) measurements, we know that

\[
\left| \frac{\partial \ln K_{\text{dp}}}{\partial P} \right| = \frac{1}{2} \frac{\partial \ln (T_1 T)^{-1}}{\partial P} \leq 4.8 \times 10^{-3},
\]

so that \( \partial \ln K_{\text{dp}} / \partial \ln V \ll 2 \) and in a naive picture where \( \partial \ln K_{\text{dp}} / \partial P \) is mainly due to a reduction of the density of states at the Fermi level, we expect this quantity to be positive. One obtains

\[
2.5 \leq \frac{\partial \ln K_{\text{orb}}}{\partial \ln V} \leq 3.5.
\]

This is much larger than, and of different sign to the values mentioned by Kushida and Murphy (1969, 1971) in V and Nb metals. We suggest two possible origins for it. First, under
pressure the splitting of the \( d_{z^2} \) bands will increase, due to a reduction of the Van der Waals gap (Matheiss 1973). This will decrease the corresponding contribution to \( K_{\text{orb}} \), which is proportional to \( E_{k,n} - E_{k,n'} \). But the broadening of the band should be accompanied by a reduction of the density of states at Fermi level, which we know to be small, from \( T_1 \) measurements, and furthermore it will concern only the axial part of \( K_{\text{orb}} \).

Secondly, the splitting between the \( d_{z^2} \) band and the upper d-bands is determined by the relative position of the niobium and selenium atoms inside a layer, and will be rather sensitive to a change in the \( c/a \) ratio of the Se prism. An increase of 10% of the crystal-field splitting would explain the Knight shift decrease from 1 bar to 21 kbar.

Let us now examine the temperature and pressure dependence of the EFG, which is reported in table 4.

### Table 4.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \partial \ln q / \partial T \bigg</td>
<td>_{1 \text{bar}} )</td>
</tr>
<tr>
<td>( \partial \ln q / \partial T \bigg</td>
<td>_{21 \text{bar}} )</td>
</tr>
<tr>
<td>( \partial \ln V / \partial T \bigg</td>
<td>_{1 \text{bar}} )</td>
</tr>
<tr>
<td>( \partial \ln q / \partial P \bigg</td>
<td>_{77 \text{K}} )</td>
</tr>
<tr>
<td>( \partial \ln q / \partial P \bigg</td>
<td>_{298 \text{K}} )</td>
</tr>
<tr>
<td>( \partial \ln V / \partial P \bigg</td>
<td>_{298 \text{K}} )</td>
</tr>
</tbody>
</table>

If we separate the EFG, \( e_{q,i} \), into a lattice contribution \( e_{q,i} \) and an electronic contribution \( e_{q,el} \), one has:

\[
\frac{\partial \ln q}{\partial T} = 0, \quad \frac{\partial \ln q_{el}}{\partial T} = \frac{q_{el}}{q_{el}} \left( \frac{\partial \ln q}{\partial T} \right)_p - \frac{\partial \ln q}{\partial \ln V} \left( \frac{\partial \ln V}{\partial T} \right)_p.
\]

Assuming \( q/q_{el} = 2.6 \) (Torgeson and Borsa 1976) one obtains at ambient pressure \( \partial \ln q_{el} / \partial T \bigg|_V = 2.1 \times 10^{-4} \). Now \( \partial \ln q / \partial \ln V \) is equal to 2.6 (3.5) at 298 K (77 K), a value which is quite close to that of \( \eta \partial \ln K_{\text{orb}} / \partial \ln V \).

Again this cannot be explained by a variation of \( \langle r^{-3} \rangle \) which would give an opposite sign variation, and we think that it is due to a change in the \( c/a \) ratio of the Se prism inside a layer.

4.2. NMR in the PLD/CDW state

When a periodic lattice distortion accompanied by a charge density wave occurs in the crystal, the conduction electron density is spatially modulated, and so will be the quadrupole couplings experienced by Nb nuclei. Assuming that the EFG are mainly due to conduction electrons of the d-band, and using a tight-binding approximation, one can show that the change in \( e_{q}(\mathbf{R}) \) at site \( \mathbf{R} \) is proportional to the change in the electronic density averaged in the Wigner–Seitz cell, \( \Delta \rho(\mathbf{R}) \). A local modulation of the Knight shift \( K(\mathbf{R}) \) will also occur which is more difficult to compute, but which should be, at least for the core polarisation contribution, proportional to \( \Delta \rho(\mathbf{R}, E_p) \).

In any case, we shall assume that both the Knight shift and the EFG distribution exhibit the same symmetry as the charge distribution, and compute the corresponding lineshape \( g(v) \) in several cases.
(i) a single incommensurate CDW:
\[ \Delta v(R) = \Delta v \cos(K_0 \cdot R) \]

(ii) a triple incommensurate CDW:
\[ \Delta v(R) = \Delta v \sum_{i=1}^{3} \cos(K_i \cdot R + \phi_i). \] (6)

According to Moncton et al. (1975) we shall investigate the situation where
\[ K_1 = \frac{1}{3}a_1(1 - \delta), K_2 = \frac{1}{3}a_2(1 - \delta), K_1 + K_2 + K_3 = 0, \]
\[ \phi_1 = \phi_2 = \phi_3 = 0, 2\pi/3 \text{ or } \pi/2 \] (Wilson et al. 1975) \( a_1 \) and \( a_2 \) are the reciprocal vectors of the hexagonal plane lattice and \( \delta \) measures the incommensurability.

(iii) a triple commensurate CDW:
\[ \Delta v(R) = \Delta v \sum_{i} \cos(K_i \cdot R + \phi) \]

where \( K_i = a_1/3, K_2 = a_2/3 \) and \( K_1 + K_2 + K_3 = 0. \)

Elementary analytical calculations, assuming a continuous distribution of nuclei in the plane shows that:

(i) \( g(v) \) is a symmetric function with two infinite square root singularities located at \( v_r = v/\Delta v = \pm 1 \).

(ii) \( g(v) \) exhibits two step singularities at \( v_r = 3 \) and \( v_r = -1.5 \) and an infinite singularity at \( v_r = -1 \) (BJMR 1976).

(iii) Here \( g(v) \) is a sum of delta functions located at
\[ v_r = 3, 0, -1.5 \quad \phi = 0 \]
\[ v_r = 0, \pm 1.5 \quad \phi = 2\pi/3 \]
\[ v_r = 0, \pm \sqrt{3}/2, \pm \sqrt{3} \quad \phi = \pi/2. \]

These lineshapes must of course be convoluted with the dipolar broadening which we know to be of the order of 10 G. So as soon as \( \Delta v \) is larger than 20 G, one cannot distinguish between commensurate and incommensurate structure.

As already pointed out (BJMR 1976) experimental results (Figures 1 and 4) clearly show that the frequency distribution due to Knight shift \( (H_0 || c \text{ axis}, (\frac{1}{2} \rightarrow -\frac{1}{2}) \text{ transition}) \) and EFG distribution below the onset temperature \( T_0 = 33 \text{ K} \) corresponds to case (ii), that is a triple incommensurate PLD/CDW with an infinite number of inequivalent sites. This rules out any interpretation in terms of two inequivalent sites and also the possibility that neutron results could be due to three types of domains with single CDW of different \( q \) vectors.

At 21 kbar, the evolution of the lineshape of the \( (\frac{1}{2} \rightarrow -\frac{1}{2}) \text{ transition} \) below the onset temperature \( T_0 = 26 \text{ K} \) shows that the symmetry of the CDW is still triple and incommensurate. At this stage, two questions deserve to be discussed: how far the value of \( \delta \) which measures the incommensurability, will be reflected on the lineshape, and how the observed NMR spectra can be reconciled with a description of the incommensurate phase in terms of discommensurations (McMillan 1976). Computer simulation performed over 25 000 atomic sites does not show any dependence of the lineshape on \( \delta \) values in the range 0.01–0.05 assuming a local change of frequency \( \Delta v(R) \) given by equation (6).

As far as discommensurations are concerned, one expects to observe the superposition of the frequency distribution calculated for incommensurate CDW with a small number of
discrete lines of dipolar width, especially at \( v_z = 0 \). This is not the case in our experiment, but it may be due to the fact that \( \delta \) is too large in this system, that is to say the area where the PLD/CDW is commensurate concerns too few nuclei.

It should be noticed that in 2H-TaSe\(_2\), Borsa et al (1976) did not observe a clear modification of the \(^{77}\text{Se}\) spectrum at the ICDW–CCDW transition. But their experiment was not really performed on a single crystal, and the anisotropic shift of the \(^{77}\text{Se}\) could have led to extra difficulties.

Let us turn now to the amplitude of the EFG and KS distribution and their temperature dependence. In figure 8, we have plotted \( \Delta K(T)/\Delta K(4.2\text{K}) \), \( \Delta q(T)/\Delta q(4.2\text{K}) \), where \( 4 \Delta K(T) (\Delta q(T)) \) is the distance between the two main singularities of the KS (EFG) distribution. Also shown are the normalised value \( \eta \) of the atomic displacement deduced from neutron scattering measurements of Moncton et al (1975) and its squared value \( \eta^2 \).

In the usual PLD/CDW theory (Overhauser 1968, McMillan 1975) both the atomic displacement and the amplitude of the CDW are proportional to the order parameter of the phase transition. This is in good agreement with the temperature dependence of the EFG distribution, which is similar to that of \( \eta \) and confirms that \( \Delta q(R) \) is proportional to \( \Delta \rho(R) \), the average change in the electronic density in the atomic cell. Now \( 3\Delta q(4.2\text{K}) \) is proportional to the maximum value of \( \Delta \rho(R) \). Assuming \( \delta q/q = \delta n/n \), where \( n \) is the number of d-electrons within the atomic cell, and \( n \sim 1 \) we deduce the maximum value of electron redistribution within the atomic cell \( \Delta n_{\text{max}} = 0.09 \) with \( \Delta q_{\text{max}} = (108 \pm 5) \times 10^{22} \text{ cm}^{-3} \), in agreement with the assertion of Rice and Scott (1975) that a small number of electrons is concerned by the CDW.

![Figure 8. Temperature dependence of the amplitude of the KS and EFG distribution in reduced units below \( T_0 \) as a function of \( T/T_0 \). The triangles are for \( \Delta q(T)/\Delta q(4.2\text{K}) \), the squares \( \Delta K(T)/\Delta K(4.2\text{K}) \). The open circles represent the neutron data of Moncton et al \((I/I_0 = \eta^2(T))\) and the full circles represent \([I(T)/I_0]^{1/2}(\eta(T))\).](image)

At 21 kbar, the amplitude of the distribution is reduced in the same ratio as the transition temperature \( T_0 \); that is the amplitude of the CDW is proportional to the gap opened at the Fermi surface which itself is proportional to \( T_0 \) as expected in a mean-field theory.

Let us now turn to the Knight shift distribution. In a recent paper Stiles and Williams (1976) pointed out that the KS distribution was proportional to the square of the CDW amplitude, and their conclusion was also true for the order parameter of the transition. They based their interpretation on two arguments. The first one, related to the lineshape, has no validity since we have shown that a frequency shift linear with the amplitude of a triple incommensurate CDW leads to a lineshape in perfect agreement with experiments. The
second one is based on the similarity of the temperature dependence of the KS distribution and the square of the atomic displacement $\eta^2$ deduced from neutron data. As a matter of fact, our data show the same behaviour, as is shown in figure 8. But as already mentioned in our previous paper, the determination of $\Delta K(T)$ is disturbed by the existence of a small inhomogeneous broadening of the $\left(\frac{1}{2} \rightarrow -\frac{1}{2}\right)$ transition present at all temperatures. Although the authors claim that the width of their distribution extrapolates to zero with the magnetic field, the data of their figure 3 rather suggest a quadrupolar inhomogeneous broadening of the order of 3 G.

At the present time, it is difficult to conclude whether or not the KS distribution is really proportional to $\eta^2$, and measurements in higher magnetic fields, in order to minimise the quadrupole broadening due to crystal imperfections, are required. Let us notice anyway that $3 \Delta K_{\omega}(4.2 K) = 0.1$ % represents only 14 % of the orbital component of $K_{\omega}$ which is not such a large value.

In conclusion, the comparison of the temperature dependence of the EFG with neutron data shows that the order parameter of the transition is proportional to the amplitude of the CDW, as considered by McMillan (1975). There exists a possibility that the KS distribution is proportional to the square of the CDW amplitude, as suggested by Stiles and Williams (1976), but this should be confirmed by measurements in higher magnetic fields.

We shall end this discussion of NMR properties related to the PLD/CDW below $T_0$ with a comment about the NSLR data. According to Friedel (1975) one expects a lowering of the density of states at the Fermi level at the onset of the transition, due to the opening of partial gaps associated with the PLD/CDW. This should lead to a decrease of $T_1$ $T$ below $T_0$; this was not observed within the error bars, giving an upper limit of 10 % for the change in $N(E_F)$ at the onset of the transition.

4.3. CDW and fluctuations above $T_0$

In our first paper, we mentioned the observation of a pretransitional broadening of the $\left(\frac{1}{2}, -\frac{1}{2}\right)$ transition (figure 1) which we were unable to ascribe either to dynamical fluctuations of the CDW, that is the appearance of a central peak when approaching $T_0$ (Bhatt and McMillan 1975) or to static fluctuations induced by impurities. Such a pretransitional broadening was also observed by Valic et al (1974) and extensively studied by Stiles and Williams (1976) who interpreted it as dynamical fluctuations on the basis of its temperature dependence. Nevertheless nothing but a measurement of transverse nuclear spin–spin relaxation time could decide if this was really a dynamic broadening. At the same time, such dynamical fluctuations should give a large contribution to $T_1$ as soon as the crystal is no longer in the particular orientation $H_0||c$. The purpose of this section is to reexamine these data in the light of new measurements of $T_2$ and $T_1$ above the transition temperature, which demonstrate the predominance of the role played by impurities.

A dynamical CDW fluctuation at site $R_i$, $\delta \xi(R_i, t)$ will induce an EFG tensor fluctuation $\delta V_{ij}(R_i, t) = \lambda \delta \xi(R_i, t)$. We shall assume that $\langle \delta V_{xx} + \delta V_{yy} + \delta V_{zz} \rangle = 0$ and that $\delta V_{xx} = \delta V_{yy}$. In this case, the Hamiltonian described by equation (1) remains valid if one replaces $\omega_Q(R_i)$ by $\langle \omega_Q(R_i) \rangle + \delta \omega_Q(R_i, t)$ and $\theta_i$ by $\langle \theta_i \rangle + \delta \theta_i(t)$. Above $T_0$, $\langle \omega_Q(R_i) \rangle$ and $\theta_i$ have the constant value measured in absence of the CDW. For $\langle \theta_i \rangle = 0$, $H_0||c$ CDW fluctuations will strongly affect the linewidth of the transitions $(m \rightarrow m - 1)$ $(m \neq 1/2)$, but the effect on the NSLR will be small; only the local fluctuations of $\theta_i$ will significantly contribute to $(T_1)^{-1}$ and

\[ \text{In that case the lineshape should possess infinite singularities at } \nu_2 = 0 \text{ and } 1, \text{ and step singularities at } \nu_2 = 2.25 \text{ and } 9, \text{ which is hardly distinguishable from our interpretation.} \]
we know that the static distribution of $\theta_i$ at 0 K is very small, since the quadrupole contribution to the broadening of the $(\frac{1}{2} \rightarrow -\frac{1}{2})$ transition below $T_0$ is negligible. On the other hand at the 'magic angle orientation' the effects on the NSLR should be as important as the linewidth broadening.

Assuming $\zeta_q(t)$ is a Gaussian stationary process, and $\sum_q \langle \zeta_q(t)^2 \rangle$ is temperature independent, one can show (Abragam 1961) that the spin–spin relaxation rate $T_2^{-1}$ is proportional to $\sum_q S(q, 0)$ the Fourier transform at zero frequency of $\langle \zeta(R, t), \zeta(R, 0) \rangle$. From Bhatt and McMillan's (1975) calculations it turns out that this quantity $\sum_q S(q, 0)$, should diverge as $(T - T_0)^{-1}$ which is the observed temperature dependence of the pretransitional broadening. Of course, the approximation $T_2^{-1} \propto \sum_q S(q, 0)$ will break down close to the transition since we do not expect $\langle \zeta^2(R, t) \rangle$ to become larger than the maximum amplitude of the CDW at zero temperature.

In the case of static fluctuations induced by impurities, the broadening is no longer homogeneous and we do not expect $T_2^{-1}$ to be proportional to the linewidth of the transition. On the contrary, the existence of an inhomogeneous broadening on the microscopic scale will decouple neighbouring spins, and $T_2^{-1}$ will become smaller than the dipole natural linewidth. Let us try to calculate in that case the temperature dependence of the linewidth. From McMillan (1975), the charge perturbation around an impurity located at the origin can be written as:

$$\Delta \rho(R) = \sum_i \cos(q_i \cdot R) K_0(R/A)$$

where $K_0$ is a special Bessel function and $\lambda$ is the coherence length proportional to $(T - T_0)^{-1/2}$. Assuming again $\Delta \omega_0(R_i) = \alpha \Delta \rho(R_i)$, the second moment of the resonance line in a dilute alloy can be written (Winter 1971)

$$M_2 = c \sum_i [\Delta \nu(R_i)]^2 + c^2 \left[ \sum_i \Delta \nu(R_i) \right]^2$$

where $c$ is the impurity concentration, and $\Delta \nu(R_i)$ the frequency shift at site $R_i$. In our case this leads to:

$$M_2 \sim c\alpha^2 \int_0^\infty [\Delta \rho(R)]^2 \, d^2 r = A\lambda^2 + \text{higher powers of } \lambda.$$  

Consequently, the linewidth should vary as $\lambda$, that is like $(T - T_0)^{-1/2}$. $T_2$ measurement at 40 K, where the linewidth is about 30 G gives a value of 240 μs which corresponds to a homogeneous linewidth of 0.6 G. This definitely proves that the pretransitional broadening we observed above $T_0$ is due to static impurity-induced fluctuations, and not to dynamical ones. As the broadening we observe has the same temperature dependence, and the same magnitude as those observed by Stiles and Williams (1976) we conclude that these authors also observed static fluctuations ($\tau_c < T_2$) induced by impurities.

An extra proof of the static and inhomogeneous character of this pretransitional broadening is the low value of $(T_1 T)^{-1}$ measured at the magic angle orientation of the crystal, whereas in the extreme narrowing limit, we should observe $T^{-1} = \gamma \Delta H - T_2^{-1} \text{dipolar}$. Let us now come to the effect of the dynamic fluctuation on the NSLR. As already stated, we expect no effect in the orientation $H_0 || e$ which is the case within the error bars. At the magic angle, we expect an extra contribution to the relaxation rate given by $T_2^{-1} \propto \sum_q S(q, \omega_n) \sim \langle \delta \omega_0 \rangle^2 \tau_c$. The lack of precision of the measurements, which were performed
only at a few temperatures, does not allow a clear answer. It seems nevertheless that at 33 K there could be a contribution which is at most 50 s⁻¹, which would lead to a correlation time \( \tau_c \approx 10^{-10} \) s for \( \langle \delta \omega_0^2 \rangle^{1/2} = 9 \times 10^5 \) rad s⁻¹, deduced from the low-temperature limit.

As for the soft modes associated to the CDW below \( T_0 \) and observed by Raman scattering (Tsang et al 1976, Steigmeyer et al 1976) one must notice that their amplitude decreases proportionally to their frequency. So, if we call \( \omega_n \) the mode frequency far from \( T_0 \), \( \omega_n \) the nuclear frequency and \( \tau \) the relaxation time of the mode given the half-width of the Raman line, we get:

\[
T_1^{-1} \approx \langle \delta \omega_0^2 \rangle \left( \frac{\omega(T)}{\omega_0} \right)^2 \frac{\tau}{(\omega(T) - \omega_0)^2 \tau^2 + 1}
\]

which is easily seen to be negligible.

In conclusion we can say that the pretransitional broadening observed above \( T_0 \) on the \((m \to m - 1)\) transition \((m \neq \frac{1}{2})\) is due to static fluctuations induced by impurities, in spite of the purity of the sample (resistivity ratio of 60). The temperature dependence of the broadening, which behaves like \((T - T_0)^{-1}\), is not understood. This experiment demonstrates the very strong interaction of CDW fluctuation with impurities, and raises the question whether diffuse x-ray or neutron scattering observation above the onset of the PLD distortion in low-dimensional systems are not due to such impurity mechanism.

5. Conclusion

We have used the pulsed NMR technique on the \(^{93}\text{Nb}\) nuclei between 4.2 K and 273 K at ambient pressure and under hydrostatic pressure of 21 kbar, in order to get information on the band structure of 2H-NbSe₂ and the PLD/CDW state in the crystal.

A careful analysis of the Knight shift, susceptibility and nuclear spin–lattice relaxation data supports the value of 2-4 eV per atomic spin for \( N(E_F) \), the density of states at Fermi level. Our previously reported \( T_1 \) \( T_1 \) value 500 ± 100 ms K was confirmed by measurements at the magic angle. We found an important orbital contribution to the Knight shift, in agreement with the band structure calculations of Matheiss (1973).

We observed an unusual large and negative pressure dependence of the Knight shift, \( \delta \ln K / \delta \ln V = -5 \) accompanied by a small variation of \( N(E_F) \), that we interpret as a variation of the orbital contribution partly due to the change in the splitting between the \( d_{z^2} \) and the upper \( d \)-bands, correlated with a change in the \( c/a \) ratio inside a layer. The onset of the incommensurate PLD/CDW at \( T_0 = 33 \) K is accompanied by drastic modifications in the NMR spectra. A distribution of EFG occurs in the crystal, the amplitude of which is proportional to the amplitude of CDW (or to the lattice distortion) which is the order parameter of the transition; this was determined by comparison with neutron results. The corresponding lineshape for each \((m \to m - 1)\) transition reflects the local symmetry of a triple incommensurate PLD/CDW and rules out any interpretation in terms of a finite number of different sites. The maximum amplitude of electron redistribution within an atomic cell was determined equal to 9%. No evidence was found for the existence of discommensuration, but this point remains unclear.

A Knight shift distribution also occurs; at the difference of the EFG distribution, its amplitude could be proportional to the square of the order parameter, as recently suggested by Stiles and Williams (1976). But this should be confirmed by measurements in higher magnetic field and remains theoretically unexplained.
Measurements at 21 kbar show the occurrence of a triple incommensurate CDW at $T_0 = 26$ K. The amplitude of the CDW is proportional to $T_0$, as expected.

Our NSLR time measurements show that the change in $N(E_F)$ in the temperature range 10–120 K and between 1 and 21 kbar is smaller than 10%. This fixes an upper limit for the lowering of the density of states due to the opening of the partial gap at the Fermi surface at the onset of the PLD/CDW (Friedel 1975).

As far as CDW fluctuations are concerned, we have shown that the pretransitional broadening observed above $T_0$ in our experiment, and presumably in those of Stiles and Williams (1976) was due to static fluctuations induced by impurities, despite the high purity of the sample. The $(T - T_0)^{-1}$ behaviour of this broadening remains unexplained, but these results demonstrate the very strong coupling of CDW fluctuations with impurities and would suggest care be taken with diffuse x-ray or neutron scattering observation in low-dimensional systems above the onset of a PLD.

Finally, we suggest the same experiment should be performed on $^{51}$V nuclei in the system VSe$_2$ (Thompson and Silbernagel 1976, Williams 1976), where the symmetry of the CDW is different, the amplitude larger, $(T_0 \approx 100$ K) and the possibility exists for an incommensurate–commensurate transition, which would allow the study of the discommensurate state (McMillan 1976).

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