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^{77}Se NMR study of the charge density wave state in 2H-$NbSe_2$ and 1T-VSe_2

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Abstract. ^{77}Se NMR spectra of single-crystalline 2H-$NbSe_2$ and 1T-VSe_2 have been measured in the temperature range 7–295 K. For both compounds the NMR lineshape is strongly affected by the phase transition to the charge density wave (CDW) state at $T_0 = 31$ K and 110 K, respectively. The temperature dependence of the normalized CDW amplitude (order parameter of the phase transition) is obtained from the width of the Knight shift distributions below T_0. For 2H-$NbSe_2$ the type of phasing of the locally commensurate CDW state is determined from the combined analysis of the ^{77}Se and ^{93}Nb NMR spectra measured on the same sample.

1. Introduction

The layered dichalcogenides 2H-$NbSe_2$ and 1T-VSe_2 exhibit structural phase transitions accompanied by charge density waves (CDWs) at temperatures $T_0 \approx 30$ K and 110 K, respectively. For both compounds the low-temperature phase is incommensurate according to the diffraction data [1–3]. However, as has been shown by McMillan [4], far from T_0 such a phase may in fact consist of locally commensurate domains. Nuclear magnetic resonance (NMR) provides a convenient microscopic probe of the local charge modulation. Since the NMR frequency strongly depends on the electron density near a nucleus, the NMR spectrum can give direct information on the distribution of CDW amplitudes at nuclear sites. The aim of the present work is to study the CDW states in 2H-$NbSe_2$ and 1T-VSe_2 by ^{77}Se NMR lineshape measurements.

The shape of ^{93}Nb NMR spectra in 2H-$NbSe_2$ has been shown to be consistent with the locally commensurate orthorhombic CDW state within each Se–Nb–Se layer [5, 6]. The existence of locally commensurate domains in 2H-$NbSe_2$ has also been confirmed by the electron microscopy study [7]. However, the phasing of charge density waves with respect to the lattice cannot be determined unambiguously from ^{93}Nb NMR measurements alone. In principle, it is possible to determine the type of the CDW phasing by comparing the shapes of ^{93}Nb and ^{77}Se NMR spectra [8]. However, the low-temperature ^{77}Se NMR spectra of 2H-$NbSe_2$ recorded by Borsa *et al* [9] in the field of 22 kG appear to be poorly resolved. In order to improve the spectral resolution, in the present work we study ^{77}Se NMR lineshapes in higher magnetic field (79.9 kG). Comparison of the ^{77}Se and ^{93}Nb NMR spectra measured

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on the same sample allows us to determine the type of phasing of the locally commensurate CDW state in 2H-$NbSe_2$.

The CDW state in 1T-VSe_2 shows a number of unusual features. According to the diffraction experiments [2, 3, 10], the superstructure formed in 1T-VSe_2 below $T_0 \approx 110$ K is commensurate in the plane of the layers (with a 4×4 unit cell), but incommensurate in the perpendicular (c axis) direction. In some samples of 1T-VSe_2 an additional phase transition near 80 K has been found [10]. At this transition the amplitude of one of the three charge density waves goes to zero ($3q \rightarrow 2q$ transition). The period of the superstructure in c axis direction also changes at this transition; however, it remains incommensurate. At present there is no direct experimental information on the phasing of CDWs in different layers of 1T-VSe_2. Possible types of phasing have been determined in the framework of Landau theory taking into account interlayer interactions [11, 12]. In principle, these theoretical results can be tested using NMR measurements. However, the ^{51}V NMR experiments on 1T-VSe_2 single crystals [12, 13] could not resolve any fine structure of the lines in the CDW state. Previous ^{77}Se NMR experiments on 1T-VSe_2 were restricted to the Knight shift measurements on powder at $T \geqslant 100$ K [14]. In the present work we report the results of high-field NMR studies of ^{77}Se lineshapes in single-crystalline 1T-VSe_2 in both the normal and CDW states.

2. Experimental details

The preparation of 2H-$NbSe_2$ and 1T-VSe_2 single crystals has been described in [5] and [13], respectively. Typical dimensions of the crystals were about $5 \times 5 \times 0.05$ mm^3. For NMR measurements 10 single-crystalline platelets were stacked with their c axes parallel to each other.

NMR measurements were performed on the modernized Bruker SXP pulse spectrometer. The magnetic field $\boldsymbol{H}$ of 79.908 kG was produced by an Oxford Instruments superconducting solenoid. The ^{77}Se NMR spectra were recorded by Fourier transforming the spin echo signals with $\boldsymbol{H}$ parallel and perpendicular to the c axis. For linewidths exceeding 50 kHz the spectra were obtained by superimposing a number of Fourier spectra excited at different frequencies.

3. Results and discussion

3.1. 2H-$NbSe_2$

In the normal phase ($T \geqslant T_0$) the ^{77}Se NMR spectrum consists of a single symmetric line, as expected for the nuclear spin $I_{Se} = \frac{1}{2}$. The position of this line strongly depends on the angle θ between $\boldsymbol{H}$ and the c axis. The isotropic (K_{iso}) and axial (K_{ax}) components of the Knight shift obtained from NMR spectra at $\theta = 0$ and 90° are found to be temperature dependent: at 295 and 35 K, respectively, $K_{iso} = 0.281\%$ and 0.324%, and $K_{ax} = 0.056\%$ and 0.064%. These results are in good agreement with those reported by Borsa *et al* [9].

Below the CDW onset temperature $T_0 = 31$ K the ^{77}Se NMR line broadens and shows the asymmetric structure. The experimental lineshapes are shown in figure 1. The observed changes in the lineshape can be attributed to the spatial modulation of the Knight shift. For transition metal dichalcogenides the resonance frequency ν at a nuclear site $\boldsymbol{R}$ can be written in the linear and local approximation [15] as

$$\nu(\boldsymbol{R}) = \nu_0 + \nu_1 \sum_{j=1}^{3} \cos(\boldsymbol{q}_j \cdot \boldsymbol{R} + \phi_j) \tag{1}$$

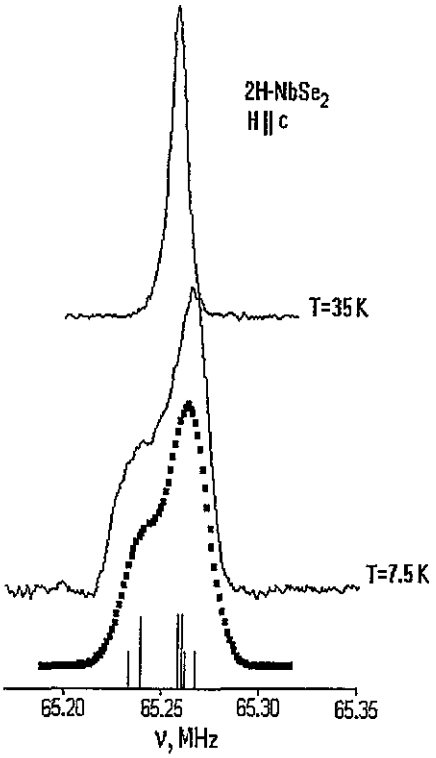

Figure 1. Experimental ^{77}Se NMR lineshapes for 2H-$NbSe_2$ at 35 and 7.5 K (above) and the simulated low-temperature lineshape (below). The simulation uses the CDW phase parameters obtained from the analysis of ^{93}Nb NMR spectra [5]. Vertical bars show the positions and relative intensities of six components in the simulated lineshape.

where ν_0 is the NMR frequency corresponding to uniform electron density, ν_1 is the modulation amplitude proportional to the CDW amplitude, q_j are the CDW wave vectors along the three equivalent ΓM directions of the Brillouin zone, and ϕ_j are the CDW phases. The origin is assumed to be at an Nb site. As can be seen from equation (1), the temperature dependence of the width of ν distribution gives direct information on the temperature dependence of the CDW amplitude. Figure 2 shows the temperature dependence of the normalized excess linewidth in the CDW state. The data on the normalized widths of the ^{93}Nb Knight shift and electric field gradient distributions from [5] are also included for comparison. It can be seen that both the ^{77}Se and ^{93}Nb data points lie close to a single curve representing the temperature dependence of the CDW amplitude.

The ^{93}Nb NMR studies [5, 6] have shown that the experimental lineshapes can be accounted for only if the local commensurability of the CDW state in 2H-$NbSe_2$ is assumed, i.e.

$$q_1 = \tfrac{1}{3}K_1 \qquad q_2 = \tfrac{1}{3}K_2 \qquad q_3 = -(q_1 + q_2) \tag{2}$$

where K_1 and K_2 are the reciprocal lattice vectors for a single layer. In this case the distribution of ν consists of a number of separate lines, their positions and relative intensities being determined by the phasing of the triple CDW state. According to the phenomenological theory of CDW in 2H structure [8], three types of the CDW phasing are possible. One of these types corresponds to the hexagonal symmetry of the CDW state within a layer ($\phi_1 = \phi_2 = \phi_3$; $\alpha\alpha$ type in the notation of [16]). The other two types are orthorhombic

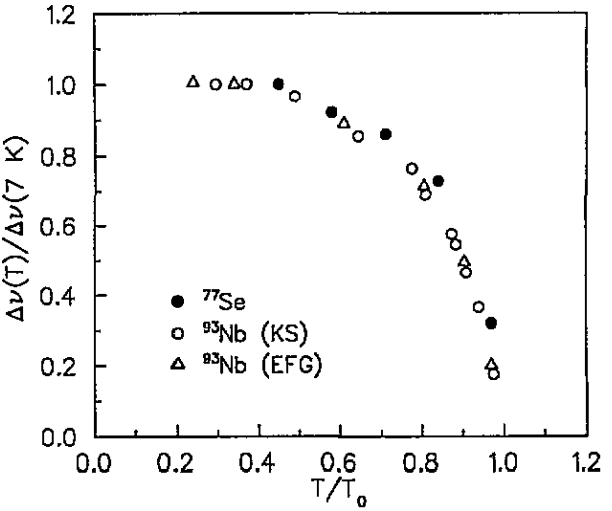

Figure 2. Temperature dependence of the normalized widths of the ^{77}Se and ^{93}Nb Knight shift distributions and the the electric-field-gradient distribution on ^{93}Nb in 2H-$NbSe_2$. The ^{93}Nb data are taken from [5].

with $\phi_2 = \phi_3$, $\phi_1 = \phi_{2,3} + \Delta\phi$. For non-interacting layers $\Delta\phi = 2\pi/3$ ($\beta\beta$ type) or $-2\pi/3$ ($\gamma\gamma$ type). For interacting layers the value of $\Delta\phi$ may deviate from $2\pi/3$ or $-2\pi/3$. We shall still define states with such deviations as $\beta\beta$ type or $\gamma\gamma$ type, respectively. This notation is broader than that introduced in [16, 17]. On the $\Delta\phi$ scale $\alpha\alpha$ states form a boundary between $\beta\beta$-type and $\gamma\gamma$-type states. $\delta\delta$-states ($\Delta\phi = \pi$) discussed by Wilson [17] represent the other boundary between $\beta\beta$- and $\gamma\gamma$-type states. Table 1 shows the expected relative intensities of inequivalent NMR lines of both ^{93}Nb and ^{77}Se for different types of CDW state. For example, for the $\alpha\alpha$ type of phasing the ^{77}Se NMR spectrum is expected to be split into three lines with relative intensities 1:1:1 for all values of the common phase angle. The ^{93}Nb NMR data [5, 6] rule out the possibility of $\alpha\alpha$-type phasing in 2H-$NbSe_2$, being consistent with $\Delta\phi = 140°$ or $-140°$. However, the ^{93}Nb NMR data do not allow to distinguish between two signs of $\Delta\phi$, i.e. between $\beta\beta$- and $\gamma\gamma$-type CDW states. On the other hand, as can be seen from table 1, the ^{77}Se NMR frequency distributions for $\beta\beta$- and $\gamma\gamma$-type states are essentially different. The difference becomes more evident if we take into account that for non-interacting $\gamma\gamma$-type layers (6:1:1:1 splitting) the line with the maximum intensity should always be centred at the unshifted frequency ν_0. For weakly interacting layers the degeneracy is partially lifted; however, the maximum of the frequency distribution is still expected to be very close to ν_0. In contrast, the experimental lineshape (figure 1) in the low-temperature phase shows a maximum which is strongly shifted with respect to its position in the normal phase. It should be noted that such a shift cannot result from the temperature dependence of ν_0 since the density of electron states at the Fermi level has been found to be nearly unchanged at the phase transition in 2H-$NbSe_2$ [6, 18]. Thus even a qualitative consideration of the data allows us to choose the $\beta\beta$ state as the preferred type of CDW phasing in 2H-$NbSe_2$. A typical frequency distribution for the $\beta\beta$-type state consists of two separate groups of lines, one of which is above ν_0 and the other one is below ν_0.

In order to make the analysis more quantitative, we have simulated the ^{77}Se NMR lineshape in the low-temperature phase. Since the spectral resolution for ^{77}Se is still not

Table 1. Expected relative intensities of inequivalent NMR lines of Nb and Se for different types of locally commensurate CDW states in 2H-$NbSe_2$. For each type of CDW state the results for non-interacting layers and interacting layers (in brackets) are shown. (Based on results of [8].)

Type of CDW state	Nb	Se
$\alpha\alpha$	6:1:1:1	1:1:1
	(6:1:1:1)	(1:1:1)
$\beta\beta$	1:1:1	1:1:1
	(2:1:2:1:2:1)	(2:1:2:1:2:1)
$\gamma\gamma$	1:1:1	6:1:1:1
	(2:1:2:1:2:1)	(2:2:2:1:1:1)

as good as for ^{93}Nb NMR, we restrict ourselves to investigating whether the CDW phase parameters found for ^{93}Nb [5, 6] can also describe the ^{77}Se lineshape. The best description of the ^{93}Nb lineshapes has been obtained with $\Delta\phi = 140°$ and $\phi_{2,3} = 2°$ [5, 6]. Because of the symmetry properties of equation (1) this solution is in fact a generator of 12 solutions having 60° periodicity in $\phi_{2,3}$ and both signs of the $(\Delta\phi, \phi_{2,3})$ combination. These solutions correspond to four physically inequivalent CDW states, since a 120° phase shift is equivalent only to a change in the numbering of the three charge density waves. As discussed above, comparison with the ^{77}Se data allows us to choose the positive sign of $\Delta\phi$. However, the 60° periodicity in $\phi_{2,3}$ is retained since a 60° phase shift in $\phi_{2,3}$ results in the sign reversal of all $\nu(\boldsymbol{R}) - \nu_0$ shifts, and we cannot relate unambiguously the sign of $\nu(\boldsymbol{R}) - \nu_0$ with the sign of the deviation of electron density at R from its average value [5]. Therefore the combined analysis of ^{93}Nb and ^{77}Se NMR spectra still cannot distinguish between the two CDW states characterized by the phase parameters $\Delta\phi = 140°$, $\phi_{2,3} = 2°$ and $\Delta\phi = 140°$, $\phi_{2,3} = -58°$. We have simulated the ^{77}Se NMR lineshape on the basis of equations (1) and (2) using $\Delta\phi = 140°$, $\phi_{2,3} = 2°$. The background broadening of spectral components is assumed to be Gaussian. The simulated lineshape is included in figure 1. As can be seen from this figure, the CDW phase parameters found for ^{93}Nb NMR can also give a satisfactory description of the ^{77}Se lineshape in the low-temperature phase. The background broadening yielding such a good agreement appears to be 30% higher than the experimental ^{77}Se NMR linewidth above T_0. The additional broadening may be ascribed to defect-induced phase fluctuations [19] in the CDW state.

It is interesting to compare the CDW phase parameters found for 2H-$NbSe_2$ with those for the related compound 2H-$TaSe_2$ having the commensurate low-temperature CDW state. The best ^{77}Se NMR data for 2H-$TaSe_2$ have been obtained by Pfeiffer *et al* [20]. Taking into account the 60° periodicity in $\phi_{2,3}$, our results for the CDW phasing appear to be close to solution 5 of [20] ($\Delta\phi \approx 150°$, $\phi_{2,3} \approx -55°$ at 60 K) and to the CDW phase parameters derived from the analysis of the electron diffraction intensity data for 2H-$TaSe_2$ by Bird *et al* [21] ($\Delta\phi = 160°$, $\phi_{2,3} = 50°$ in our notation). This means that the types of CDW phasing in 2H-$NbSe_2$ and 2H-$TaSe_2$ are similar. In both cases the CDW state is orthorhombic within a single layer, the value of $\Delta\phi$ being between $2\pi/3$ and π.

3.2. 1T-VSe_2

At room temperature the ^{77}Se NMR spectrum consists of a single line with a full width at half maximum of about 10 kHz. The dependence of the position of this line on θ is considerably stronger than in the case of 2H-$NbSe_2$. Because of the strong θ dependence of the shift the measured linewidth is found to have a contribution related to a slight misalignment of

c axes of individual crystals in the stack. The temperature dependence of the isotropic and axial components of the Knight shift obtained from NMR spectra at $\theta = 0$ and 90° is shown in figure 3. The sign of the normal state temperature dependence of both K_{iso} and K_{ax} is the same as for 2H-$NbSe_2$. As can be seen from figure 3, both $K_{iso}(T)$ and $K_{ax}(T)$ show maxima near $T_0 \approx 110$ K. The decrease in K_{iso} and K_{ax} below T_0 may be ascribed to the drop in the density of electron states at the Fermi level revealed by the ^{51}V NMR experiments [13, 14, 22]. It should be kept in mind, however, that the Knight shift values shown in figure 3 are derived from the positions of line maxima, and therefore below T_0 they may be affected by the onset of the resonance frequency distribution. Comparison of our Knight shift results with those reported for powder at $T \geqslant 100$ K [14] shows that the Knight shift values of [14] are very close to our values of $K(\theta = 90°)$. This means that, contrary to the expectations of the authors of [14], they measured in fact not K_{iso}, but $K(\theta = 90°)$ values. In the presence of a strong Knight shift anisotropy it may be difficult to notice in the powder spectrum a small 'step' (corresponding to $\theta = 0$) which is far away from the main 90° peak.

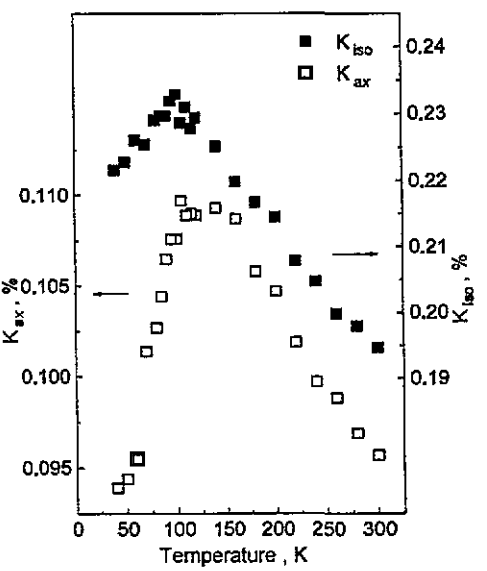

Figure 3. Temperature dependence of the isotropic and axial components of the ^{77}Se Knight shift in 1T-VSe_2.

The temperature dependence of the ^{77}Se linewidth at $H \parallel c$ is shown in figure 4. Below 110 K a strong line broadening is observed. The transition to the CDW state is also accompanied by changes in the lineshape. In particular, the lineshape becomes asymmetric with the stretched high-frequency slope (figure 5). It is interesting to note that the shape of the ^{77}Se line is similar to that of the central ^{51}V line [12] in the CDW state of 1T-VSe_2. As in the case of ^{51}V NMR, the analysis of the lineshape in terms of CDW phasing seems to be impossible since no fine structure of the line can be resolved. The absence of any fine structure of the NMR frequency distribution is probably an intrinsic property of 1T-VSe_2, since all possible types of CDW stacking in this compound result in a large number of closely spaced spectral components [12].

As can be seen from figure 4, a certain line broadening appears already above T_0. Similar line broadening above the transition point has been reported for ^{51}V quadrupole

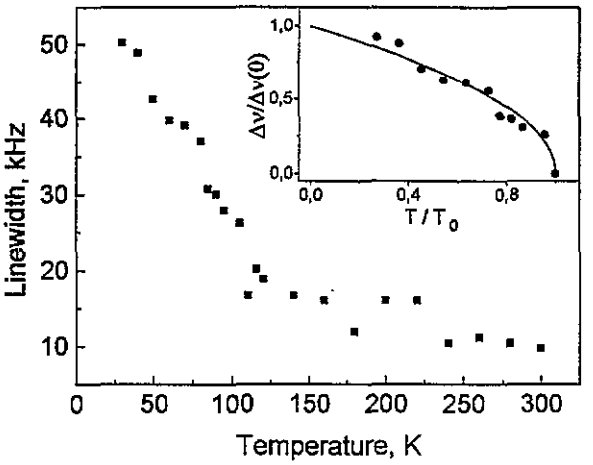

Figure 4. Temperature dependence of the ^{77}Se linewidth in 1T-VSe_2 at $H \| c$. Inset: temperature dependence of the normalized excess linewidth in the CDW state. The solid line shows the power law with the exponent of 1/2.

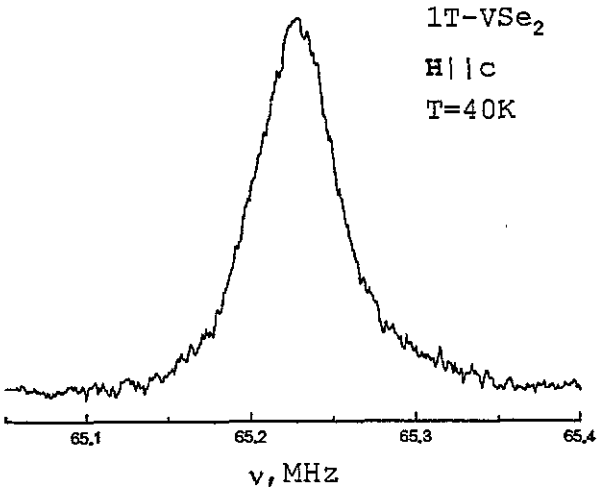

Figure 5. The experimental ^{77}Se NMR lineshape in 1T-VSe_2 at 40 K.

satellites in 1T-VSe_2 [12, 13]. It can be ascribed to defect-induced lattice distortions which are expected to be enhanced near the transition point [18].

The inset of figure 4 shows the temperature dependence of the normalized excess linewidth below T_0. As in the case of ^{51}V NMR [12], this temperature dependence can be described by the power law with the exponent of $\frac{1}{2}$. Note that the temperature dependence of the normalized excess linewidth in the CDW state of 1T-VSe_2 significantly differs from that of 2H-$NbSe_2$ (figure 2) where the linewidth changes strongly near T_0 but remains nearly constant below $T/T_0 = 0.5$. This means that the behaviour of the CDW amplitude (order parameter of the phase transition) in these two compounds is quite different.

The $3q \rightarrow 2q$ phase transition in 1T-VSe_2 is expected to result in strong changes in the lineshape. In particular, the NMR lineshape in the $2q$ phase should be symmetric [11, 12]. However, we have not found any changes in the lineshape near 80 K that could be

ascribed to the $3q \rightarrow 2q$ transition. This is consistent with the ^{51}V results [12] indicating the absence of the $3q \rightarrow 2q$ transition in our sample. Studies of the phase diagram of 1T-VSe_2 based on Landau theory [11, 12] have shown that the occurrence of the $2q$ phase strongly depends on parameters of interlayer interaction. On the other hand, crystals of 1T-VSe_2 are always formed with deviations from the exact stoichiometry [23]. They can be more accurately described as V_xVSe_2, where x represents a fraction of V atoms intercalated between the layers. It is natural to assume that the presence of even a small fraction of V atoms between the layers may significantly change the interlayer interaction. Therefore the occurrence of the $3q \rightarrow 2q$ transition is expected to depend on the concentration of such defects. However, at present it is not clear whether an increase in x stabilizes or suppresses the $3q \rightarrow 2q$ transition. In order to clarify this, further systematic studies of the samples with different values of x are required. Since V atoms intercalated between the layers have localized magnetic moments [23], their concentration can be estimated from magnetic susceptibility measurements. For our sample such an estimate results in the value $x = 0.007$ [13].

4. Conclusions

Comparison of the ^{77}Se and ^{93}Nb NMR spectra measured on the same sample of 2H-$NbSe_2$ allows us to conclude that the CDW phasing in the locally commensurate domains corresponds to the orthorhombic $\beta\beta$-type state with $\Delta\phi = 140°$. The shapes of both ^{77}Se and ^{93}Nb NMR lines at low temperatures can be satisfactorily described by the same CDW phase parameters.

For 1T-VSe_2 such an assessment of the CDW phase parameters appears to be impossible because of the absence of well resolved spectral features in the low-temperature NMR lineshapes of both ^{77}Se and ^{51}V. The temperature dependence of the CDW amplitude for 1T-VSe_2 can be described by the power law with the exponent of $\frac{1}{2}$. The ^{77}Se NMR line in 1T-VSe_2 shows also some pretransitional broadening. We have not found any signs of the additional $3q \rightarrow 2q$ transition in our sample. The occurrence of this transition may be related with concentration of intrinsic defects—V atoms intercalated between the layers.

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