Interplay of charge density waves, disorder, and superconductivity in $2H$-TaSe$_2$ elucidated by NMR

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Single crystals of the pristine and 6% Pd-intercalated $2H$-TaSe$_2$ have been studied by means of $^{77}\text{Se}$ nuclear magnetic resonance (NMR). The doping and temperature dependence of the $^{77}\text{Se}$ spectrum, with an unexpected line narrowing upon doping, unravels strong correlated lattice distortions far above the transition temperature of the charge density wave (CDW) order, thereby evidencing a strong-coupling CDW mechanism in $2H$-TaSe$_2$. Further, the $^{77}$Se spin-lattice relaxation rate $T_1^{-1}$ as a function of temperature shows that a pseudogap behavior dominates the low-energy spin excitations even within the CDW phase, and gets stronger along with superconductivity upon Pd doping. Our NMR data suggest that lattice-commensurate, not incommensurate, CDW is the main competitor of superconductivity in the transition metal dichalcogenides.

Charge density wave (CDW) order in two dimensions, together with its relationship to superconductivity, has been a fascinating and central issue in the layered transition metal dichalcogenides (TMDs) [1–3], and even more so owing to remarkable similarities with high-$T_c$ copper-oxide superconductors (cuprates) [4]. Electronic phase diagrams in many metallic TMDs suggest that the emergence or enhancement of superconductivity is closely related to CDW order, although the relationship between the two phenomena remains unclear. Another particularly interesting feature in TMDs is the presence of a pseudogap regime [5–8] which involves strange-metal behavior in the normal state. The origin of the pseudogap is often ascribed to a CDW instability [6, 9], an argument also put forward for cuprates [10–12]. Hence the deep understanding of the nature and origin of the CDWs in TMDs may provide vital clues to the mechanism for high-temperature superconductivity.

$2H$-TaSe$_2$ is one of the intensely investigated TMDs, as it develops a series of fascinating phases: an unusual metallic state with a pseudogap at high temperatures is followed by an incommensurate CDW (iCDW) transition at $T_{\text{icDW}} \sim 120$ K, a lock-in transition into the commensurate CDW (cCDW) at $T_{\text{cCDW}} \sim 90$ K, and a superconducting (SC) transition at $T_c = 0.14$ K [13]. No consensus has been reached on whether the CDW order is of weak-coupling nature, driven by Fermi-surface nesting [14–16], or of more local strong-coupling character [17–19].

Since the two distinct CDW transitions successively occur at much higher temperatures than $T_c$, it may be possible to establish a relation between CDW and superconductivity by tuning control parameters such as pressure or doping. Recently, it has been demonstrated that Pd intercalation leads to the dramatic enhancement of $T_c$ up to 3.3 K near an optimal Pd content of $\sim 8\%$ at which the cCDW completely vanishes while the iCDW transition remains robust [20], as shown in Fig. 1. Being motivated by the strong effect of Pd doping on superconductivity and the commensurate CDW in $2H$-Pd$_x$TaSe$_2$, we carried out $^{77}$Se nuclear magnetic resonance (NMR) in the pristine and 6% Pd-intercalated $2H$-TaSe$_2$. Our data demonstrate that the major driving force for the CDW formation is strong electron-phonon coupling. Pd doping introduces both changes to the electronic structure and random pinning centers, together being responsible for the strong smearing and suppression of the lock-in transition to the cCDW phase as well as for the strengthening of the pseudogap behavior on top of the substantial increase of $T_c$.

**Experimental.** Single crystals of $2H$-Pd$_x$TaSe$_2$ ($x = 0$ and 0.06) were grown by the chemical vapor transport method as described in detail in Ref. [20]. It has been confirmed that the Pd intercalation does not alter the $2H$ structure of the pristine compound, as drawn in the inset of Fig. 1. $^{77}$Se (nuclear spin $I = 1/2$) NMR was carried out in pristine and 6% Pd-intercalated $2H$-TaSe$_2$ single crystals ($\sim 0.7 \times 0.5 \times 0.1 \text{ mm}^3$) at an external magnetic field of 15 T, and in the range of temperature 4.2–300 K. The samples were oriented using a go-
FIG. 1. Phase diagram of $2H$-Pd$_x$TaSe$_2$. The CDW transitions $T_{iCDW}$ and $T_{cCDW}$, and the superconducting transition $T_c$ (multiplied by 5) were extracted from Ref. [20]. The empty squares for $x > 0.04$ suggest that $T_{cCDW}$ is not clearly defined. The red arrows on the top denote the compositions of the samples measured in this work. Inset shows the crystal structure of $2H$-TaSe$_2$, which is preserved with the Pd intercalation. The dashed lines represent the unit cell.

NMR linewidth. The temperature dependence of the full width at half maximum (FWHM) of the $^{77}$Se spectrum for $H \parallel ab$ is presented in Fig. 2(a). For the pristine sample, the FWHM gradually increases with lowering temperature and undergoes a notably large change roughly below $\sim 150$ K, essentially saturating below $T_{iCDW}$. With 6% Pd intercalation, the FWHM is considerably reduced – see the $^{77}$Se spectra at 10 K presented in the inset of Fig. 2(a) – while maintaining a temperature dependence similar to that of the pristine sample. Since the FWHM of an NMR line in a non-magnetic material is a measure of local inhomogeneity, the narrowing of the $^{77}$Se line indicates that the inhomogeneity decreases with Pd doping. Such a reduction of an NMR linewidth with doping is extremely unusual, considering that any dopants inevitably introduce chemical disorder typically leading to a large NMR line broadening. Indeed, the in-plane resistivity $\rho_{ab}$ in $2H$-TaSe$_2$ significantly increases with 6% Pd doping, Fig. 2(b), reflecting the increase of lattice disorder by doping. Hence, the evolution of the NMR linewidth in $2H$-TaSe$_2$ cannot be explained by lattice defects alone, but must be related to CDW phenomena.

A remarkable feature found in Fig. 2(a) is that the FWHM is reduced by Pd doping in the whole temperature range by the nearly same amount. This implies that correlated local lattice distortions exist even at temperatures far above $T_{iCDW}$ [21], and the amplitude of the distortions is suppressed with Pd doping. These local distortions seem to gradually evolve into the long-ranged CDW state when cooling from elevated temperatures to below $T_{iCDW}$. This is clearly inconsistent with a conventional, i.e., weak-coupling, CDW mechanism, in which lattice distortions develop only below the CDW transition tem-
perature and thus a CDW-related linewidth reduction could occur only inside the CDW phase. Therefore, we conclude that the CDW transition in 2H-TaSe$_2$ is not primarily driven by electronic Fermi-surface nesting of Peierls type [14, 15], but rather by local electron-phonon coupling [17–19] leading to a strong-coupling CDW mechanism with a large fluctuation regime [3, 22, 23]. Note that Fermi-surface properties will still play a role in strong-coupling scenarios.

To fully understand the evolution of the NMR linewidth, a more detailed consideration of doping and disorder effects is required. First, lattice distortions at temperatures far above $T_{\text{iCDW}}$ could be expected to rapidly fluctuate in time. However, the presence of any lattice defects will lead to pinning, such that distortions become inhomogeneous but static (at least on the NMR time scale), realizing local patches of CDW order. While the density of pinning centers is low in the pristine sample, leaving sharp iCDW and cCDW transitions essentially intact, it will strongly increase with Pd doping. This leads to a significant smearing of both CDW transitions in line with random-field pinning, consistent with experimental results [20]. Second, the intrinsic periodicity of the CDW can be expected to compete with the spatial arrangement of dense pinning centers, resulting in an overall suppression of the distortion amplitude and strongly inhomogeneous distortion patterns even at low $T$, naturally accounting for the nearly indefinable cCDW transition near 6% Pd intercalation [20]. Third, Pd doping is known to produce modifications to the electronic band-structure [16], weakening nesting conditions and making bands more three-dimensional. This likely reduces the effects of electron-phonon coupling and contributes to suppressed lattice distortions.

Knightshift. The Knight shift $K$ of the $^{77}$Se spectrum, which is equivalent to the Pauli spin susceptibility in a non-magnetic metal, is presented in Fig. 2(c) as a function of temperature for $H \parallel ab$. We also measured $K$ for $H \parallel c$ at low temperatures to check its anisotropy. Whereas the weak temperature dependence of $K$ reflects the metallic nature of the two samples, a small drop of $K$ is clearly observed below $T_{\text{iCDW}}$ similarly for the pristine and doped samples. This indicates that the iCDW transition involves a partial gap opening at the Fermi level whose magnitude is nearly unchanged with Pd doping. Specifically, the Fermi surface nesting may partially contribute to the CDW transition, although it is unlikely the main driving force [17]. The clear increase of $K$ in the 6% Pd-doped sample indicates that the density of states at the Fermi level, $n(\epsilon_F)$, is notably enhanced with Pd doping, consistent with the reported band-structure modifications [16]. An enhanced $n(\epsilon_F)$ is naturally compatible with the increased $T_c$ [20].

Spin dynamics. Having established a lattice-driven CDW mechanism and its suppression by Pd intercalation, we now turn to low-energy spin dynamics probed via the spin-lattice relaxation rate $T_1^{-1}$ which is very sensitive to quasiparticle excitations near the Fermi level in metals. Figures 3(a) and (b) present $T_1^{-1}$ and $(T_1 T)^{-1}$, respectively, as a function of temperature in 2H-Pd$_x$TaSe$_2$ ($x = 0$ and 0.06) measured at 15 T parallel and perpendicular to the c axis. $(T_1 T)^{-1}$ decreases with decreasing $T$, indicating the presence of the pseudogap at the Fermi level. Lines are guides to eye.

\[\begin{align*}
(T_1 T)^{-1} & = \frac{1}{T_1} - \frac{1}{T_1 T} = \text{const., should hold} \\
T_1 & \propto T
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ing accompanies the enhancement of $n(\epsilon_F)$, but contrasts with the weakening of lattice distortions and the CDW. These observations strongly suggest that the pseudogap can be directly linked neither to Fermi surface nesting [8, 16] nor to static lattice distortions above the transition as expected in a strong-coupling CDW scenario [22]. Possibly, the pseudogap is instead related to dynamically fluctuating CDW; such fluctuations of the CDW may also be responsible for the strange metallic behavior characterized by the linear variation of resistivity with temperature [7, 20].

**Discussion.** We now try to synthesize our observations into a coherent picture. The intrinsically strong electron-phonon coupling rules much of the phenomena in 2H-TaSe$_2$ and determines the correlation between CDW, pseudogap, and superconductivity in the phase diagram, Fig. 1. Electron-phonon coupling produces correlated lattice distortions whose amplitude gets reduced by Pd intercalation. Pd intercalation also destroys the cCDW state by strong random-field-type pinning, while it enhances the pseudogap behavior, and strongly enhances the superconducting $T_c$.

The maximum of $T_c$ is obtained at a doping level where the cCDW phase has disappeared, but the iCDW phase continues to be present. The strongly enhanced $T_c$ in the light of a weakly doping-dependent $T_{c,iCDW}$ suggests that it is the commensurability of the CDW that competes with superconductivity, rather than CDW ordering itself. Conversely, superconductivity and incommensurate CDW are not mutually exclusive in nature [25].

Indeed, other superconducting TMDs are also well understood in line with this reasoning. The isostructural 2H-NbSe$_2$ and 2H-NbS$_2$ [1] in which the cCDW transition is absent, exhibit $T_c = 7.2$ K and 6.3 K, respectively, much higher than 0.14 K and 0.8 K of the Ta counterparts in which the cCDW is present [26]. Furthermore, suppressing $T_{c,iCDW}$ has a negligible effect on $T_c$ in 2H-NbSe$_2$ [27], consistent with a weak correlation between iCDW and superconductivity as in Fig. 1. In contrast, suppressing $T_{c,CDW}$ either by doping or by external pressure in 1T polytypes mostly induces a substantial increase of $T_c$ — 1T-TaSe$_2$ [28], 1T-TaS$_2$ [29, 30], 1T-TiSe$_2$ [31, 32], and 1T-VSe$_2$ [33], as it precisely did in 2H-TaSe$_2$. Paretistically, we note that the cCDW phase in 1T-TaS$_2$ is known to be a Mott insulator, suggesting that electron correlations may be also important for superconductivity in TMDs.

Interestingly, a similar discussion appears sensible for cuprates as well. In La-based cuprates, for instance, the CDW commensurability plays an important role in stabilizing static charge stripe order [34] which competes with superconductivity, with a particularly strong suppression of $T_c$ near 1/8 hole doping. In contrast, the incommensurate CDW order seen in other cuprate families leads to little or no suppression of superconductivity [35], pointing to the important role of the commensurability in competing with superconductivity.

Lastly, the fact that both the pseudogap behavior and superconductivity are boosted by Pd doping may suggest that the two phenomena are linked in that CDW fluctuations contribute to both. We note that the very different temperature scales of pseudogap and superconductivity in 2H-TaSe$_2$ appear to rule out that the pseudogap is a state of preformed pairs, as discussed for cuprates [36–38], but suggest that the pseudogap is a phenomenon distinct from superconductivity [39, 40].

**Summary.** We carried out $^{77}$Se NMR measurements in 2H-Pd$_x$TaSe$_2$ ($x = 0$ and 0.06). Local lattice distortions as precursor of CDW formation exist at even at room temperature, likely arising from strong electron-phonon coupling, evidencing a strong-coupling CDW mechanism in 2H-TaSe$_2$. Pd intercalation reduces these lattice distortions, due to a combination of strong pinning disorder and modifications to the band-structure, and leads to a suppression of the commensurate CDW. At the same time, the low-energy electronic density of states is enhanced, as is the pseudogap as seen in the spin-lattice relaxation rate. We propose that quenching the commensurability of the CDW is a crucial factor for the enhancement of $T_c$.

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[26] Although the lock-in transition has not been reported for 2H-TaS2, the local charge density at 4.2 K is found to be commensurate by NMR [41].