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Charge-density-wave transport in hydrogen-doped NbSe₃

R. E. Thorne, T. L. Adelman, J. McCarten, M. Maher, and A. McDowell

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

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The effects of hydrogen impurities on charge-density waves (CDW's) in NbSe₃ have been investigated. Hydrogen can be introduced interstitially into NbSe₃ in concentrations of at least several atomic percent with no effects on the crystal structure and only weak effects on the Peierls transitions. The threshold electric field E_T for charge-density-wave depinning and the inverse of the residual resistivity ratio r_R^{-1} increase monotonically with H concentration for small concentrations. For concentrations above 1.5 at.%, E_T and r_R^{-1} exhibit a plateau, which we interpret as evidence for H clustering or ordering. Several different measurements indicate that CDW interaction with H is roughly 100 times smaller than with Ta, the most weakly perturbing substitutional impurity in NbSe₃. Hydrogen doping should thus allow study of CDW's in a new, very weakly pinned regime. In nominally pure NbSe₃ prepared by standard methods, H is present in larger quantities than any other impurity, and may play an important role in memory effects and long-time-scale fluctuation phenomena.

Charge-density waves (CDW's) which form below Peierls transitions in quasi-one-dimensional metals such as NbSe₃ give rise to some of the most remarkable transport effects ever discovered.¹ These effects include nonlinear dc conduction above a threshold electric field E_T of millivolts per centimeter,^{2,3} frequency-dependent ac conduction at megahertz frequencies,^{2,4} coherent current oscillations in response to dc excitations,³ mode-locking phenomena in response to combined ac and dc excitations,⁵ and a host of memory effects. All of these effects are a consequence of phase-dependent CDW interaction with impurities.

In the phenomenological model of Fukuyama, Lee, and Rice⁶ (FLR), the effects of impurities depend upon their strength (given by the impurity potential V_0); their concentration c_i ; and the CDW's elastic stiffness, proportional to the Fermi velocity v_F . The ratio of the CDW-impurity interaction energy to the elastic energy required for CDW deformations over lengths comparable to the average impurity separation,

$$\epsilon = V_0 \rho_1 / c_i \hbar v_F,$$

determines the nature of the impurity-pinned state.⁷ (Here ρ_1 is the amplitude of the CDW charge modulation.) For $\epsilon \gg 1$ ("strong" pinning), the impurity potential dominates, and the CDW phase is pinned at each impurity. For $\epsilon \ll 1$ ("weak" pinning), the elastic energy dominates, and the CDW phase is pinned on lengths much greater than the average impurity spacing by fluctuations

in the impurity potential. Qualitatively different CDW behavior is predicted in these two regimes. For example, in strong pinning, $E_T \propto c_i$, while in weak pinning, $E_T \propto c_i^2$.

Several studies of the effects of substitutional impurities such as Ta (which is isoelectronic with Nb) and Ti (a charged impurity) on CDW's in NbSe₃ have been reported.⁸⁻¹³ Ti acts as a strong pinning center, while results for Ta have been inconclusive with both weak and strong pinning behavior having been observed. This is not surprising, since estimates of ϵ for typical Ta concentrations are near 1; large Ta concentrations necessary to make $\epsilon \ll 1$ result in threshold fields which, because of Ohmic heating, are too large to measure.

Here, we report preliminary results for the effects of an interstitial impurity, hydrogen, on CDW's in NbSe₃. Hydrogen impurities interact with the CDW roughly 100 times more weakly than Ta, and can be introduced into NbSe₃ crystals in very large concentrations. Hydrogen doping thus provides a very weakly pinned regime for the study of CDW's.

Single crystals of hydrogen-doped NbSe₃ were prepared using the following method. Niobium hydride (NbH_x) was formed by cooling 99.9% pure Nb powder from 600°C to room temperature in an H₂ atmosphere. The mole fraction x was determined by measuring pressure changes due to absorption of H. This NbH_x was then used with stoichiometric amounts of Se in closed-ampoule vapor transport growth to yield NbSe₃. Most of the hydrogen is liberated from the NbH_x at temperatures well

below the growth temperature; vapor transport growth thus proceeds in an atmosphere of H_2 and H_2Se gases. The advantages of this preparation method include uniform doping levels and precise control over the amount of H introduced into the growth ampoule. Twenty-one growths with hydrogen mole fractions between $x=0$ and $x\approx 0.9$ were performed. Data presented here are for crystals from 14 batches prepared under identical conditions, although similar results were obtained for the other seven batches. The presence of large quantities of H did not visibly affect vapor-transport growth: Transport rates, crystal nucleation points, and crystal morphologies were similar to those observed in the absence of added H.

The amount of hydrogen incorporated into the $NbSe_3$ crystals was determined using inert-gas-fusion/thermal-conductivity analysis. As shown in Fig. 1, the H concentration in the crystals varies approximately linearly with the H mole fraction x in the NbH_x source material, with a maximum concentration of ~ 6 at.% H (per Nb) for $x\approx 0.9$. Thus, roughly 7% of the H introduced into the growth ampoule incorporates into the crystals. The gas pressure measured in the ampoule after growth also varies linearly with x , consistent with the inert-gas-fusion results. Hydrogen concentrations of a few atomic percent are also indicated by NMR measurements. Precision powder x-ray measurements show no change in peak positions or widths relative to nominally pure crystals. Thus, very large amounts of hydrogen may be incorporated interstitially into $NbSe_3$ crystals with no significant structural distortions.

The anomalies observed in the low-field dc resistivity below the Peierls transitions at $T_{P_1}\approx 145$ K and $T_{P_2}\approx 59$ K are nearly unaffected by the H doping. For H concentrations of ~ 2 at.%, the size of the anomalies is unchanged and both transition temperatures are suppressed by only about 0.3 K. In contrast, T_{P_1} and T_{P_2} are

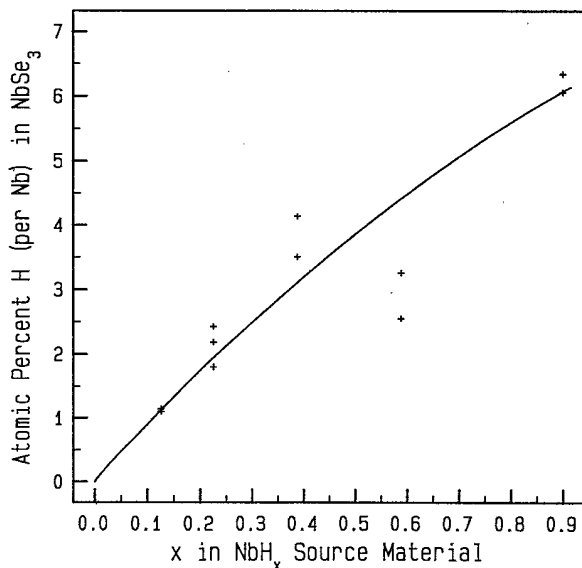


FIG. 1. Atomic present H (per Nb) in vapor-transport grown $NbSe_3$ vs H mole fraction x in the NbH_x source material. The solid line is a guide for the eye.

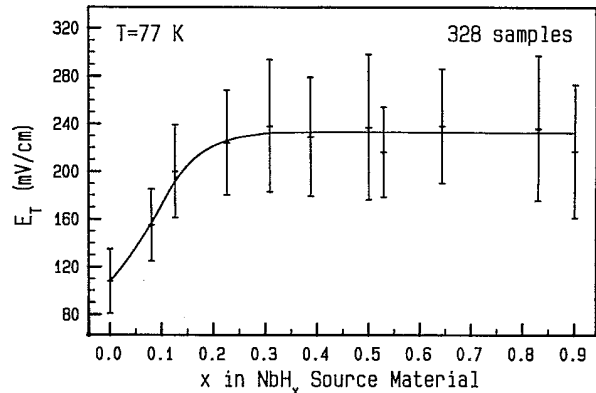


FIG. 2. Threshold electric field E_T for CDW depinning in $NbSe_3$ at 77 K vs x . The data points and error bar lengths represent the mean and twice the standard deviation of the E_T distribution for each growth. The solid line is a guide for the eye. The large widths of the E_T distributions necessitate characterization of a large number of crystals from each growth.

suppressed by ~ 10 K by Ta concentrations of only 0.5 at.%.⁹

The most frequently measured quantity for characterizing the CDW-impurity interaction is the dc threshold field E_T for the onset of CDW conduction. Previous studies of E_T in doped $NbSe_3$ have had two major deficiencies. First, only a very small number of crystals (typically 3–6) were measured from each growth batch. Second, these crystals were not screened for cross-sectional area. Crystals from a given growth batch exhibit threshold fields which vary by more than an order of magnitude. We find that most of this variation is due to differences in sample cross section, and thus to varying contributions of surface pinning¹⁴ to the measured threshold. In nominally pure $NbSe_3$, the threshold field increases rapidly with decreasing cross-sectional area A for A below about $30 \mu m^2$. Consequently, we believe that statistically significant conclusions regarding the precise functional dependence of E_T on impurity concentration cannot be drawn from these earlier studies, especially for Ta impurities. To obtain more meaningful results, we have excluded crystals with cross sections less than $30 \mu m^2$ from the analysis, and we have measured a very large number of crystals—a total of 560 from 21 growths.

Figure 2 summarizes results for the threshold field E_T at 77 K vs H mole fraction x . Measurements of E_T versus temperature indicate that the same functional form is obtained for all H dopings, so that the concentration dependence may be adequately characterized by measurements at a single temperature. For x less than 0.2 (H concentrations less than 1.5 at.%), E_T increases monotonically with increasing x , similar to the behavior observed with other impurities. However, above $x\sim 0.2$, E_T is independent of x . As shown in Fig. 3, the inverse of the residual resistivity ratio [$r_R^{-1}=R(4\text{ K})/R(300\text{ K})$], which is usually thought to reflect the impurity concentration, exhibits similar behavior. The maximum values of E_T and r_R^{-1} in hydrogen-doped $NbSe_3$ are roughly 2.5 and 1.6 times those of nominally pure material, respectively. This indi-

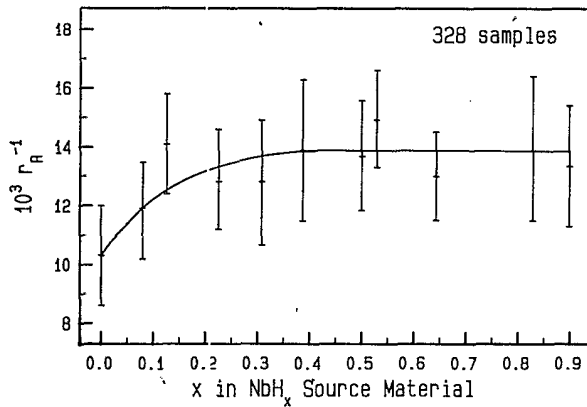


FIG. 3. Inverse residual resistivity ratio vs x . The data points and error bar lengths represent the mean and twice the standard deviation of the r_R^{-1} distribution for each growth. The solid line is a guide for the eye.

icates that the total pinning strength of the H impurities is comparable to that of the background impurities (mostly Ta), whose concentration we estimate to be ~ 1000 ppm. Since source materials much purer than those used here are available, hydrogen-dominated pinning should be readily achieved.

The reason for the saturation of E_T and r_R^{-1} is not clear at this time. One obvious possibility is that the H doping level saturates above $c_i \sim 1.5$ at.%. However, this would be inconsistent with the chemical analysis and gas pressure measurement results described earlier. In addition, these H concentrations are more than an order of magnitude below those required to fill up any interstitial site. A more likely possibility is that at concentrations above 1.5 at.% the H atoms do not act independently. The CDW is pinned by disorder, so that if the H atoms order (e.g., form pairs or clusters) additional H will not increase the pinning. Ordering effects are observed in a variety of metals for H concentrations in this range.¹⁵

One of the most interesting properties of H impurities in NbSe₃ is that their effects on single-particle and collective properties are so small. Table I compares the per-

TABLE I. Comparison between the effects of H and Ta impurities on the properties of NbSe₃. The H values are for a concentration of ~ 2 at. %.

	Ta	H	Ratio H/Ta
$\Delta T_P(K)/c_i(\%)$	20 ^a	0.15	0.75×10^{-2}
$E_T(V/cm)/c_i(\%)$	4.6 ^b 5.0 ^c 7.0 ^d	0.08	$\sim 1.3 \times 10^{-2}$
$r_R^{-1}/c_i(\%)$	0.2 ^b 0.7 ^d	0.007	$\sim 1.6 \times 10^{-2}$

^aReference 8.

^cReference 10.

^bReference 7.

^dReference 11.

impurity effects of H and Ta doping on the Peierls transition temperature T_P , the threshold field E_T , and the r_R . For all three properties, the effects of H impurities are roughly 100 times smaller than those of Ta impurities.

The weakly perturbing nature of H impurities results because they are interstitial rather than substitutional, and thus have a much smaller effect on the Nb d_{z^2} orbitals responsible for the CDW-forming bands. Preliminary NMR measurements are consistent with H occupying interstitial positions roughly 1.5 Å from a Nb atom. The trigonal Se prisms on the two CDW-bearing chains are isosceles, with the short Se-Se bond length approaching that in solid Se. We speculate that the H bonds with one of the Se's in the prism's base, relaxing the short Se-Se bond without significantly altering the charge sharing with the Nb.

What is the significance of the small hydrogen-CDW interaction? The most weakly perturbing substitutional impurity in NbSe₃ is Ta. Results for Ta doping have been ambiguous, suggesting pinning behavior intermediate between weak and strong. Hydrogen, on the other hand, has a much smaller interaction with the CDW and can be introduced into NbSe₃ crystals in very large quantities. Hydrogen doping thus permits the study of CDW's which are truly weakly pinned.

Hydrogen-doped NbSe₃ crystals exhibit a number of other interesting effects. In general, the onset of CDW conduction in H-doped crystals is sharper and shows less hysteresis than in nominally pure material, suggesting that the pinning is more uniform in the former. However, in some crystals exhibiting multiple depinnings, which are usually associated with the presence of extended defects or macroscopic crystal imperfections, the differential resistance dV/dI shows an asymmetry over a broad temperature range below T_{P2} . As shown in Fig. 4, the threshold field measured when the current is swept from negative to

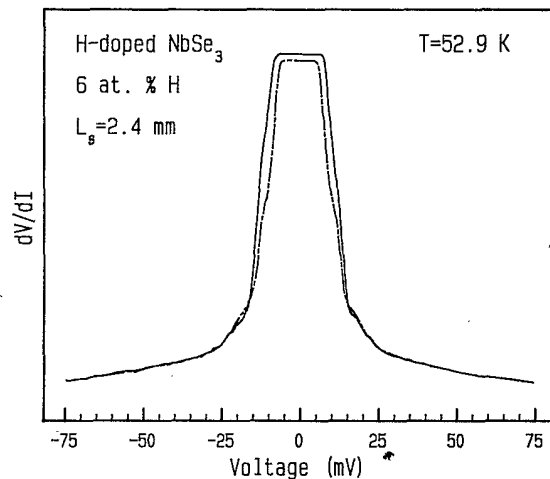


FIG. 4. Differential resistance vs voltage for a NbSe₃ crystal doped with ~ 6 at. % H. The solid line corresponds to a current sweep from negative to positive voltage, the dashed line to a sweep in the opposite direction. A second depinning occurs roughly halfway down the peak in dV/dI ; the separation between the two depinnings was clearer at other temperatures.

positive values is different from that observed for sweeps in the opposite direction. No asymmetry or hysteresis is observed when the current is always kept above or below zero. No asymmetry has been observed in crystals having dV/dI 's which decrease smoothly above threshold. Similar asymmetries have been observed in $K_{0.3}MoO_3$,¹⁶ and one interpretation is that they arise from interaction of mobile point defects with extended defects. H atoms in $NbSe_3$ may thus be somewhat mobile, leading to a time-dependent distribution of pinning centers. However, the H atoms are not as mobile as in metals such as Nb: preliminary NMR measurements show no evidence for motional narrowing of the H line at temperatures of up to 250°C.

Aside from its action as a weak pinning center, there is another good reason for being interested in the effects of hydrogen in $NbSe_3$. The fused quartz ampoules used in vapor transport growth of CDW materials contain hydrogen in the form of hydroxyl groups. When heated to high temperatures, this hydrogen (together with much smaller amounts of water vapor and oxygen) is evolved as gas from the quartz surface.¹⁷ We have measured the gas pressure inside the ampoules after growth of nominally pure $NbSe_3$. For 125-ml ampoules initially evacuated to 10^{-6} Torr, we measure pressures after growth of between 3 and 15 Torr. These pressures correspond to hydrogen

doping levels of between 0.06 and 0.3 at.%. Thus, for $NbSe_3$ crystals prepared by standard methods, hydrogen is present in larger quantities than any other impurity. CDW pinning by this hydrogen likely accounts for no more than 20% of the measured threshold in even the purest $NbSe_3$ currently available. However, if H is indeed somewhat mobile at typical measurement temperatures and moves under the influence of stresses produced by CDW deformations, it may play an important role in memory and long-time-scale fluctuation phenomena.

Further work is required to determine the mechanism by which H incorporates into $NbSe_3$ and to determine the sites which it occupies, its mobility, and the mechanism of its interaction with the CDW. The present work establishes hydrogen doping as an important new tool for study of the CDW-impurity interaction.

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