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Superconductivity in irradiated charge-density-wave compounds $2H$-NbSe$_2$, $2H$-TaS$_2$, and $2H$-TaSe$_2$

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Superconducting T_c can be increased by a low concentration, less than 1%, of irradiation-induced defects in the layered charge-density-wave (CDW) compounds $2H$-NbSe$_2$, $2H$-TaS$_2$, and $2H$-TaSe$_2$. This is due to the pinning effect of the defects which perturbs the long-range coherence of the CDW. Resistive transitions show tails below a first drop, suggesting inhomogeneous superconductivity. Such effects are proposed to be related to CDW domains.

The superconductivity in the low-dimensional synthetic metals presents a challenge for the solid-state science. Organic conductors and inorganic, pure or intercalated layer or chain compounds[1,2] offer a remarkable chemical flexibility in attempts to optimize the superconducting parameters, i.e., to increase the critical temperatures or critical fields. However, the low-dimensional character of these materials makes other ground states enter in competition with superconductivity.[3,4] A condensation of conduction electrons in charge-density waves (CDW) or spin-density waves (SDW) decreases the critical temperature considerably and even inhibits superconductivity in the most one-dimensional systems. The latter was the fate of organic conductors before the success in stabilizing superconductivity under pressure.[5] Earlier pressure had been used on the layered transition-metal dichalcogenides to reveal that the suppression of the CDW enhances superconductivity.[6] It was also observed that in the layer compounds the CDW could be perturbed by intercalation or doping, in favor of superconductivity.[7,8] Theoretical investigations on the effect of defects are in agreement with this observation: T_c is increased by scattering with nonmagnetic impurities.[9]

This competition and coexistence of superconductivity and CDW in the presence of defects is the subject of the present paper. The following results on electron-irradiated $2H$-NbSe$_2$, $2H$-TaS$_2$, and $2H$-TaSe$_2$ demonstrate that an increase of T_c, observed by resistivity, can be associated with a low concentration, of the order of $10^{-3}-10^{-2}$ atomic fraction, of irradiation-induced defects. Meanwhile, electron diffraction gives evidence of CDW distortions even in the absence of macroscopic CDW-onset transitions.

Samples of $2H$-TaS$_2$ ($T_c \sim 0.6$ K, Ref. 10), $2H$-TaSe$_2$ (0.15 K, Ref. 11), and $2H$-NbSe$_2$ (7.1 K) were grown by P. Molinié (Laboratoire de Chimie des Solides, Nantes) using the iodine transport method. They were irradiated in a Van de Graaff accelerator with 2.5-MeV electrons. Such electrons create a random, homogeneous distribution of small defects by displacing lattice atoms in elastic collisions.[12] The quantity of disorder is measured as the fraction of displaced metal atoms. A careful estimation of this quantity is possible because the magnitude of the displacement threshold energy is known.[13] On the other hand, magnetic-susceptibility measurements on a structurally analogous compound VSe$_2$, in which the displaced V atoms carry free paramagnetic moments, have confirmed this defect concentration scale.[14]

The superconducting properties were studied with resistivity measurements at low current densities (< 0.1 A/cm^2). A liquid-He cryostat with a lowest accessible temperature of 2.2 K was used and a magnetic field up to 1.85 T was available to monitor the critical-field effects. The temperature was measured with a carbon-glass resistor calibrated against the vapor pressure of liquid He. Some low-temperature resistivity curves of irradiated $2H$-NbSe$_2$, $2H$-TaS$_2$, and $2H$-TaSe$_2$ are presented in Fig. 1(a). Transitions are observed at temperatures clearly separated from the T_c values typical of pristine materials, and, in the case of $2H$-TaS$_2$ and $2H$-TaSe$_2$, well above them! The development is shown more clearly in Fig. 2 which gives the T_c's as a function of the defect concentration. The resistivity curves of Fig. 1(a) contain another important observation: The resistivity tails suggest that the superconducting state is not established in all the volume of the sample simultaneously.[15]

Further on, upper critical-field measurements, such as demonstrated in Fig. 1(b), were used to estimate the gradient dHc_2/dT for the applied field perpendicular and parallel to the layers. The results are collected in Table I where we show also the Ginsburg-Landau coherence lengths estimated according to the anisotropic theory that has been commonly applied in the case of dichalcogenides.[8,16]

Qualitatively, the increase of T_c is not very dif-

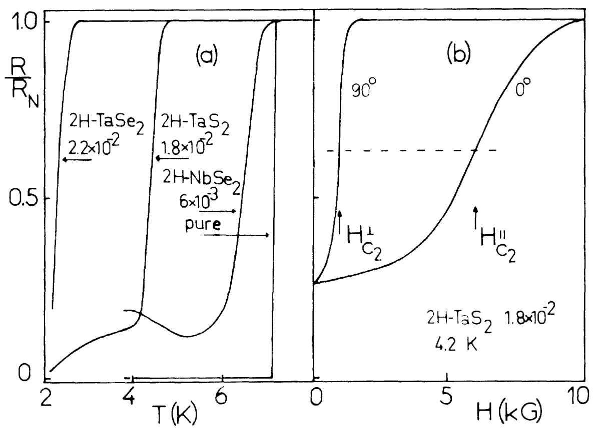

FIG. 1. Examples of the resistive superconducting transitions in pure and irradiated 2*H*-NbSe$_2$ (measured only down to 3.9 K), and in irradiated 2*H*-TaS$_2$ and 2*H*-TaSe$_2$. The defect concentrations are given as the fraction of displaced metal atoms. (a) Temperature-induced transitions. Note the considerable tails below the first drop in irradiated 2*H*-TaS$_2$ and 2*H*-NbSe$_2$. (b) Magnetic-field-induced transition for irradiated 2*H*-TaS$_2$ with the field perpendicular (90°) or parallel (0°) to crystal layers. The upper critical field is taken at the midpoint of the resistivity change.

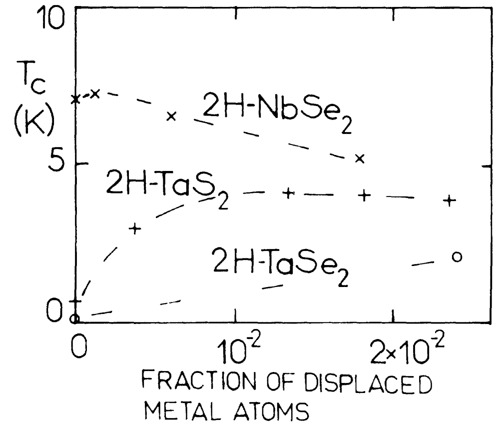

FIG. 2. Dependence of T_c on the concentration of irradiation defects. T_c is taken as the temperature at which resistivity is half of the normal-state value. The values for pure 2*H*-TaSe$_2$ and 2*H*-TaS$_2$ are from Ref. 11.

ferent from what has been observed when perturbing the CDW with other types of disorder. Intercalation[7] or doping,[8] and irradiation with 180-keV Ar ions[17] have been shown to induce similar effects. Even the resistivity tail below a first drop is often observed.[8,17] Quantitatively, however, the electron irradiation that we use reveals a completely new aspect of the problem. We observe that a quite low concentration (below 1%) of displaced metal atoms, distributed uniformly in the sample, can induce an effect comparable to the one associated with several percent of doping or intercalation species.[7,8] The bombardment with 180-keV Ar ions[17] produces damage similar to electron irradiation but only in a thin surface layer (the range is about 2000 Å) in which the displacements are very concentrated. Each atom is displaced more than ten times with the doses used in that work.

We have also followed in some detail the effect of the electron irradiation-induced defects on the CDW.[18] A first indication of the CDW amplitude should be obtained from the onset temperature T_0, that we have determined by resistivity and Hall-effect measurements. In the case of 2*H*-NbSe$_2$, T_0 decreases with a rate of 110 K/% of displaced Nb and extrapolates down to zero with a dose of about

TABLE I. T_c, upper critical-field gradients, and Ginsburg-Landau coherence lengths for irradiated 2*H*-NbSe$_2$ and 2*H*-TaS$_2$.

Compound, fraction of displaced atoms	T_c (K)	$dH_{c2}^{\perp}/dT$ (kG/K)	$dH_{c2}^{\parallel}/dT$ (kG/K)	$\xi_{\parallel}$ (0) (Å)	$\xi_{\perp}$ (0) (Å)
2*H*-NbSe$_2$	7.15	8.3	20.0	70	30
6×10^{-3}	6.65	10.0	26.7	70	26
1.8×10^{-2}	5.2	11.7	36.7	70	27
2*H*-TaS$_2$ [10]	0.6	1.13	13.1	960	80
3×10^{-3}	3.05	10	50(±10)	100	20
1.8×10^{-2}	4.20	10	75(±10)	90	12
2.3×10^{-2}	3.95	12	70(±10)	80	13

3×10^{-3}. In $2H$-TaS$_2$, the initial decrease is much slower, only about 25 K/% of displaced Ta. Moreover, T_0 never reaches zero. Instead, the transition is gradually smeared out, becoming undetectable around 1% of Ta displaced.

In spite of the disappearance of the well-defined transitions one can observe incoherent CDW distortions in both of these materials. For example, Fig. 3 shows the electron diffraction patterns obtained on $2H$-NbSe$_2$ during an *in situ* irradiation at 10 K in a 1-MV high-voltage electron microscope. Due to irradiation-induced defects the CDW diffraction satellites are broadened but the diffuse intensity persists up to doses where the macroscopic onset transition no more exists. Similar observations have been made on $2H$-TaS$_2$.[18] It is conceivable that the broadened diffraction satellites originate from a collection of CDW domains pinned to defects. Such domains have been observed directly in $1T$-TaS$_2$ in which the intensity of diffraction satellites permits imaging by dark field electron microscopy.[19]

A microstructure that consists of pinned CDW domains could explain why resistive superconducting transitions are typical of inhomogeneous materials. Variations of the amplitude of the CDW from one domain to another, and in the boundary regions, give rise to variations of the microscopic superconducting parameters. Consequently, the macroscopic properties are those of a composite, determined by percolation and tunneling between the regions with the highest T_c (Ref. 15).

It is interesting to compare our results more generally with the systems where CDW or SDW competes with superconductivity. A look at the recent literature reveals striking analogies: For example, the pure NbSe$_3$ shows typically inhomogeneous superconducting properties, incomplete resistive transitions,[20–23] and a susceptibility of a filamentary superconductor.[24] With doping[22,25] or pressure[23] it is possible to increase the T_c considerably and to obtain homogeneous superconductivity; however, radiation damage suppresses the superconductivity.[26] Examples of incomplete resistive transitions and resistive tails after a first drop can be found also in the organic systems in which the SDW competes with superconductivity.[27–29] In the organic superconductor bis-tetramethyltetraselenafulvalene hexafluorophosphate [(TMTSF)$_2$PF$_6$] the correlation between induced disorder and inhomogeneous superconductivity has been demonstrated: A stagewise resistive transition was observed after irradiation.[29]

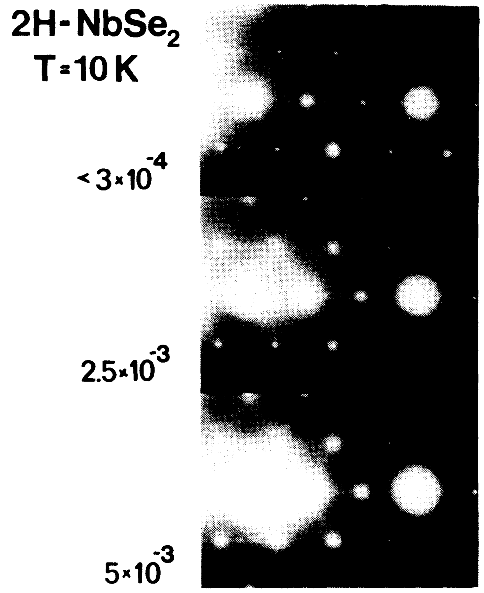

FIG. 3. A broadening of the CDW diffraction satellites in $2H$-NbSe$_2$ is observed during an *in situ* irradiation in a high-voltage electron microscope. A considerable intensity persists even when a fraction of 5×10^{-3} of Nb atoms has been displaced, in spite of the fact that the onset transition has disappeared from macroscopic properties.

These analogies with the irradiated dichalcogenides strongly suggest that the inhomogeneous superconductivity in the low-dimensional conductors can be related to the phase disorder in the CDW or SDW. In these materials lattice defects are susceptible to produce pinned domains and domain boundaries of CDW or SDW. Consequently, grains or filaments of different T_c or superconducting and normal material are formed and macroscopic superconducting properties are inhomogeneous.

Summing up, our results show that less than 1% of irradiation-induced lattice defects in the form of displaced metal atoms have important consequences on the competition of CDW and superconductivity in layered dichalcogenides. In spite of the loss of well-defined CDW onset transitions the diffraction experiments show evidence of phase-disordered CDW distortions. This is consistent with the existence of pinned CDW domains, which, in turn, might explain the very broad resistive superconducting transitions. Similar problems may be encountered in other low-dimensional conductors.

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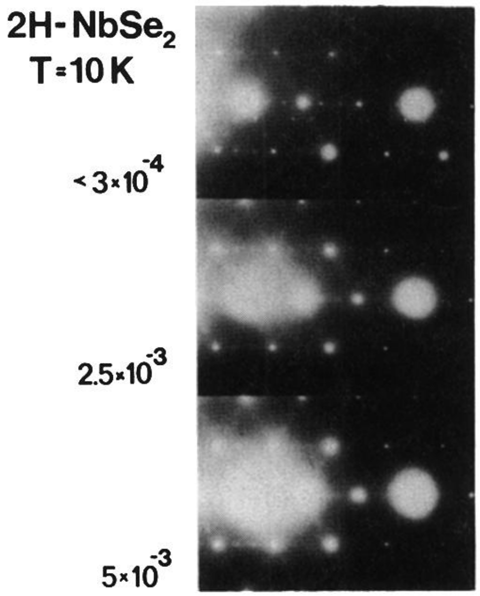

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