STM studies of Co_xNbSe_2 and Mn_xNbSe_2

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Abstract. Cobalt and Manganese intercalated $NbSe_2$ single crystals have been synthesized and characterized by DC magnetization and scanning tunnelling microscopy (STM) at low temperatures. We observed a pronounced peak effect in magnetization for both Co and Mn intercalated samples that we further investigated by low temperature STM. A structural phase transition of the vortex lattice (VL) has been observed for applied magnetic fields corresponding to the peak in magnetization.

1. Introduction

Transition metal dichalcogenides 2H-TMX_2, where TM is a transition metal and X=S, Se, or Te have been studied for decades for the coexistence and/or the interplay of different ground states such as charge-density waves and superconductivity [1]. Intercalation of various kinds of metal atoms in transition metal dichalcogenides has been explored extensively and has been used to modify and control their physical properties. However, such intercalation compounds M_xTMX_2 have been reported only for limited compositions x, such as $x = 1/2$, 1/3 and 1/4 [2].

In this paper we report on the synthesis and the characterization of Co and Mn intercalated $NbSe_2$ single crystals in the low range of intercalated atoms content. We studied the effect of the magnetic atoms intercalations on the VL, as a function of intercalated concentrations, through DC magnetization measurements and low temperature STM. A pronounced peak effect in magnetization appears in M_xNbSe_2 (with M=Co and Mn) single crystals. We studied the order-disorder transition of the VL with a low temperature STM, which allows imaging of the VL in direct space and in the presence of high magnetic fields. We find an abrupt change in the orientational order parameter of the VL, corresponding to the peak effect in magnetization.

2. Samples

The intercalated Co_xNbSe_2 and Mn_xNbSe_2 single crystals were synthesized starting from raw materials by iodine vapor transport at 900 ° C [3]. The crystal structure was verified by X-ray.

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The samples were found to be single phase with the 2H-$NbSe_2$ structure. The Co and Mn content were verified by X-ray microprobe analysis. The superconducting critical temperature was determined by SQUID magnetometry in a small applied field of 1 Oe. We found that for the concentrations studied in this paper (x<0.02 for Co_xNbSe_2, and x< 0.005 for Mn_xNbSe_2) the reduction in T_c is about 3K per at. % for Co and about 25 K per at. % in the case of Mn intercalation.

The in-plane resistivity ρ was measured by conventional dc four probe method under a current density $J = 0.1 - 0.3$ A/cm^2. Figure 1 shows the temperature dependence of the in-plane resistivity for a pure $NbSe_2$, a Co_xNbSe_2 with x=0.015 (T_c=5.7 K) and a Mn_xNbSe_2 with x=0.0016 (T_c=5.8 K) single crystals. The residual resistivity ratio (RRR= $\rho(300K)/\rho(8K)$) decreases from almost 50 in pure $NbSe_2$ crystal down to RRR=13.7 for the Mn_xNbSe_2 crystal and RRR=3.3 for Co_xNbSe_2 crystal. The inset of Figure 1 shows an enlarged plot of the resistivity ρ around T=30K for the pure $NbSe_2$ and the Mn_xNbSe_2 crystals. The resistivity of the pure sample shows a broad bump around 32K, which is believed to be caused by the CDW transition. The broad bump is shifted to lower temperature (T=23 K) in the Mn_xNbSe_2 sample and it is not observable in the Co_xNbSe_2 crystal (not reported in the inset). It has been already reported in literature [4] that this feature in the resistivity can only be observed for high quality crystals even in pure $NbSe_2$ (high values of RRR). When RRR decreases the kink in resistivity is smeared and this has been explained as an additional scattering mechanism at the CDW domains. Therefore, our data suggest that the temperature of long-range order CDW is decreased by a very small amount of Mn intercalation. On the other hand in the case of Co_xNbSe_2, being the amount of Co almost 10 times larger than the amount of Mn, there is no long range order CDW phase.

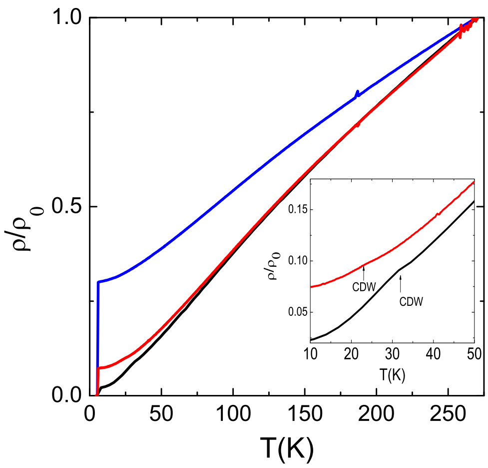

Figure 1. Temperature dependence of the resistivity ρ normalized at the value $\rho(270K)$ for a pure $NbSe_2$ crystal (black line), a Co_xNbSe_2 crystal (blue line) with x=0.015 and a Mn_xNbSe_2 crystal (red line) with x=0.0016. In the inset an enlarged view around T=30 K is reported for the pure sample (black line) and Mn intercalated one (red line).

3. Magnetization Measurements

DC magnetization measurements were performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The magnetization hysteresis loops of the Co and Mn intercalated $NbSe_2$ single crystals were measured at different temperatures and in applied magnetic fields parallel and perpendicular to the crystallographic c-axis of the single crystals.

Figure 2 shows the magnetization loops at 1.8 K, 3.6K and 4.2K for magnetic field applied parallel to the c-axis, for a Co_xNbSe_2 single crystal with x=0.015 and critical temperature

T_c=5.7K. The magnetization becomes reversible at a relatively low magnetic field, therefore the region of reversible magnetization extends for most of the mixed state. By further increasing the applied magnetic field, the magnetization becomes irreversible and then finally closes near the upper critical field H_{c2}. Since the irreversible magnetization is proportional to the critical current density of the sample, the hysteretic magnetization loop implies a peak in the critical current density close to the upper critical field. This phenomenon is known as "peak effect" and it has been reported in many type-II superconductors [5, 6, 7, 8]. However, some features appear to be peculiar. Remarkably, magnetization studies reveal that the magnetic irreversibility below the peak effect regime is higher in pure $NbSe_2$ crystals and in intercalated samples with lower concentration of cobalt. Therefore, it is not obvious that samples with higher concentration of Co, which should act as pinning centers for the VL, should show a weaker pinning at low fields. Moreover, we found that the amplitude of this peak is a non-monotonic function of the Co content (in the range of intercalation studied) and it reaches its maximum for an optimal Co content x=0.015.

Figure 3 shows the magnetization loops at 1.8 K, 3.2K and 4.2K for magnetic field applied parallel to the *c*-axis, for a Mn_xNbSe_2 single crystal with x=0.0016 and critical temperature T_c=5.8K. We obtain a similar magnitude of the peak effect with much smaller concentration of pinning centers. This implies a much stronger pinning strength of Mn compared to Co. However, the other distinct features of the peak effect attributed to Co_xNbSe_2 are not observed in this case.

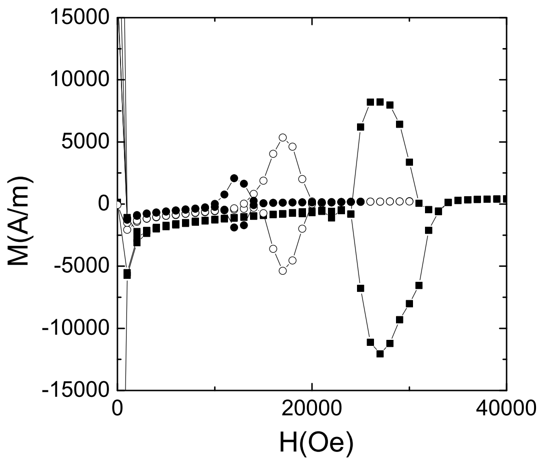

Figure 2. Magnetization of a Co_xNbSe_2 single crystal with x=0.015 at temperatures T=1.8K (■), T=3.6K (○) and T=4.2K (●). The magnetic field is applied along the c-axis of the crystal.

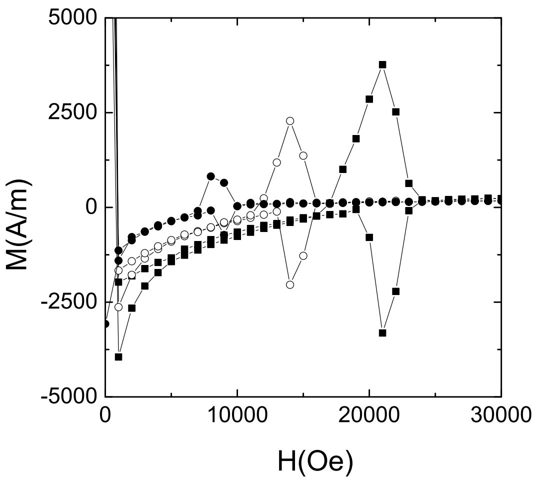

Figure 3. Magnetization of a Mn_xNbSe_2 single crystal with x=0.0016 at temperatures T=1.8K (■), T=3.2K (○) and T=4.2K (●). The magnetic field is applied along the c-axis of the crystal.

4. STM Measurements

The VL was investigated using low temperature STM at 4.2 K and in magnetic fields corresponding to the regime of the peak effect. The STM allows us to visualize the VL by mapping the tunneling differential conductance as a function of location in an applied magnetic field. In Figure 4 a set of STM images at 4.2 K and at three different magnetic fields are shown.

The measurements have been performed in zero field cooled regime. Each image corresponds to a scanning area of $375nm \times 375nm$. The images have been acquired at a voltage corresponding to the superconducting gap energy of the sample and at a tunneling current of about $10pA$. In Figure 4 we show VL images obtained on a sample of Co_xNbSe_2 with x=0.015 and at three magnetic fields: (a) H= 0.8 T, well below the onset of the peak effect region in the isothermal magnetization curve shown in Figure 2; (b) H=1.27 T corresponding at the maximum of the peak effect region; (c) H=1.32 T above the peak effect region and very close to H_{c2}. The first image Figure 4(a) shows a perfect vortex arrangement without visible distortions. At the field 1.27 T (Figure 4(b)) an abrupt change in the structure of the lattice is observed that persists in higher fields (Figure 4(c)).

In conclusion, we studied the evolution of the peak effect in M_xNbSe_2 (M=Co and Mn) single crystals as a function of the intercalated concentrations. We correlated the transition order-disorder of the VL, studied by STM, and the peak effect in DC magnetization.

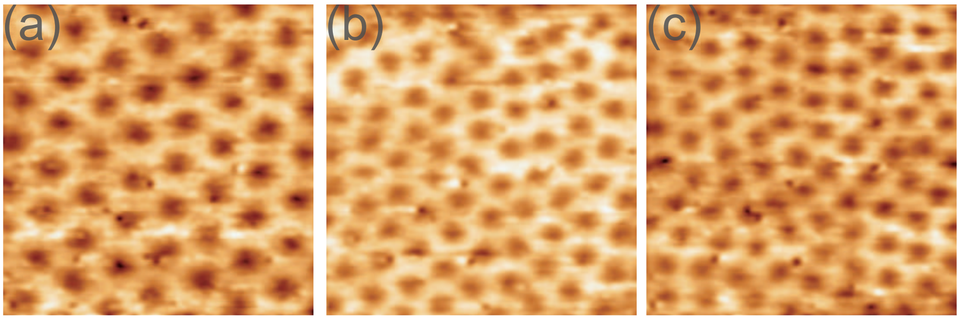

Figure 4. Sequence of STM images of the vortex lattice acquired at 4.2 K at different magnetic field applied perpendicular to the crystal surface, for a Co_xNbSe_2 single crystal with x=0.015 and T_c=5.7 K. (a) corresponds to an applied magnetic field H=0.8 T below the peak effect region in the magnetization loop reported in Figure 2 (b) H= 1.27 T, at the maximum of the peak and (c) H= 1.32 T, above the peak effect region.

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