Connection between Charge-Density Waves and Superconductivity in $NbSe_2$ †

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A study of the effect of magnetic impurities and magnetic field on the purported charge-density—wave (CDW) transition in $NbSe_2$ reveals an intriguing connection between the CDW and the superconducting states. Increasing magnetic impurity concentration results in a reduction of the transition temperature for CDW formation identical to the suppression of the superconducting T_C. A magnetic field, on the other hand, enhances the CDW transition.

The "anomalous" behavior of layered transition-metal dichalcogenides has recently been proposed to derive from the formation of charge-density waves (CDW's).[1,2] I report here two new observations concerning these CDW's which have been made in studies of the effect of magnetic impurities on the properties of one of these dichalcogenides, $NbSe_2$, namely that the T_C for CDW formation is magnetic-field dependent and that the effect of magnetic impurities on CDW formation shows behavior identical to that produced by magnetic impurities on the superconducting state.

Below room temperature $NbSe_2$ is known to undergo two phase transitions, a superconducting transition around 7.2 K and a second-order transition around 40 K which is characterized by a change from a high-temperature positive Hall coefficient to a low-temperature negative coefficient. This latter transition has been proposed to be due to CDW formation[1,2] resulting in Nb-site charge inequivalencies of as much as 5% at 4 K.[3]

I have measured the Hall coefficients in single crystals of $NbSe_2$ doped with small amounts of magnetic impurities. These crystals were prepared from powdered compounds by the standard vapor-transport mechanism.[4] Impurity concentrations quoted in this paper are those of the powdered material. Figures 1 and 2 show the variations in the Hall coefficient with temperature for samples of various impurity concentrations of iron and manganese. Values for all samples are normalized to their room-temperature values. Difficulties in measuring the size of the specimens made the determination of absolute values uncertain, but all room-temperature values of the Hall constant were on the order of 4.5×10^{-4} cm^3/C. All data were taken with the magnetic field perpendicular to the layers of the crystals. The data of Figs. 1 and 2 were taken with an applied magnetic field of 10

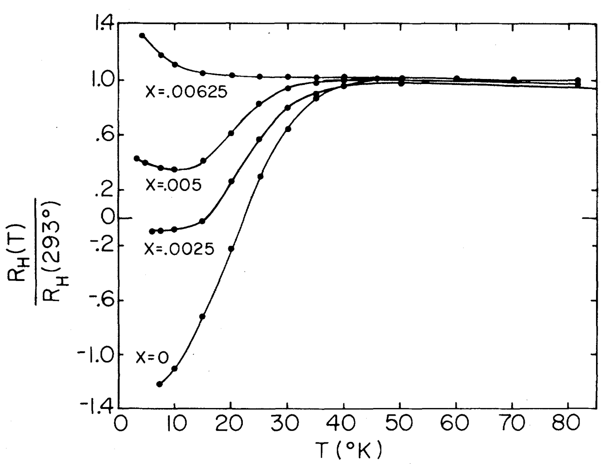

FIG. 1. Hall coefficient versus temperature for $NbSe_2$ doped with different concentrations x of iron. Values are normalized to room-temperature value. The magnetic field was 10 kOe.

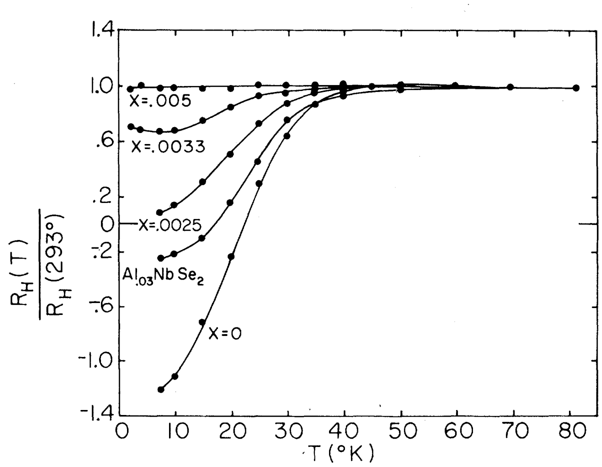

FIG. 2. Hall coefficient versus temperature for $NbSe_2$ doped with different concentrations x of manganese. Also shown are data for sample with 3 mole % of aluminum impurities. Values are normalized to room-temperature value. The magnetic field was 10 kOe.

kOe. The significant observation for both Fe and Mn impurities is that with increasing impurity concentration there is a suppression of the transition in the Hall coefficient relative to that observed for pure $NbSe_2$. Both a decrease of the temperature for the onset of the transition and a decrease in the magnitude of the change in the Hall coefficient are observed. Slightly more than 0.25 mole % of Fe impurities was necessary to suppress the sign change, while for a concentration between 0.5 and 0.625 mole % the transition is completely suppressed. For Mn impurities the suppression is greater for a given concentration with complete suppression occurring at 0.5 mole %. Also shown in Fig. 2 are data for a sample doped with 3 mole % of aluminum, a nonmagnetic impurity. It is obvious that the quenching effect of the nonmagnetic impurity is much smaller than for magnetic impurities. The increase in the Hall coefficient at low temperatures for the 0.625-mole-% Fe sample appears to be connected with some type of skew scattering mechanism possibly associated with the Kondo scattering anomaly which we have observed previously in these samples.[4] This will be reported in a future paper. It is a new and intriguing result that the CDW-induced transition is so extremely sensitive to the concentration of magnetic impurities. Such behavior is very similar to that which occurs in the suppression of the transition temperature in superconductors with the addition of magnetic impurities.

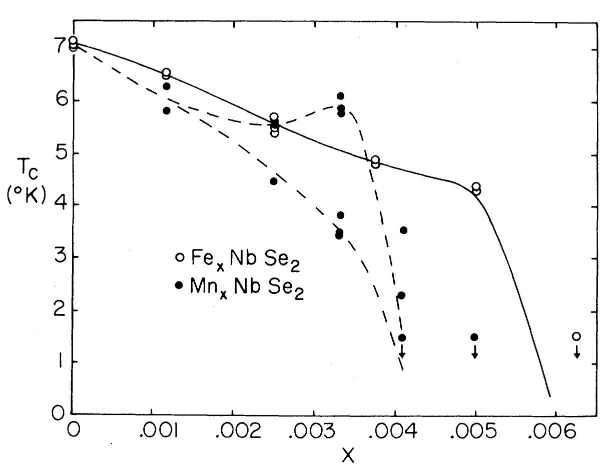

FIG. 3. Superconducting transition temperature of $NbSe_2$ doped with different concentrations of iron and manganese. Arrows indicate value was below minimum temperature achievable. For manganese doping two possible curves are shown.

In Fig. 3 is shown the superconducting transition temperature versus impurity concentration for single crystals of $NbSe_2$ doped with Fe and Mn. A rather smooth decrease in T_C is observed at low concentrations with a sharp decrease as the critical concentration for complete suppression of superconductivity is approached. Similar data for Fe impurities have been published previously.[5] Samples with Mn impurities show scattered results near the critical concentration with what would appear to be two distinct curves. This suggests that the impurities are not randomly distributed in the sample (there is other evidence for this with higher-concentration samples) although resistivity values in all samples of one concentration are the same. The peak in T_C just before the critical concentration is reached has been observed previously in Fe-, Co-, and Ni-doped samples and has been associated with a reduction in spin-flip scattering due to interactions between impurity atoms.[5] For comparison, aluminum doping results in a suppression in T_C of only 1 deg for a 3 mole % concentration. With comparison of Fig. 3 with Figs. 1 and 2, it is clear that the quenching of superconductivity and quenching of the CDW transition in $NbSe_2$ occur at approximately the same magnetic impurity concentration.

A study was made of the magnetic field dependence of the Hall coefficient for different impurity concentrations. In Fig. 4 the variation in the Hall coefficient for pure $NbSe_2$ between 1 and 12 kOe is plotted for several different temperatures. At 7.5 K there is a significant decrease in the coefficient (more negative), of about 25% between 1 and 12 kOe. At 20 K the decrease is about 50%. On the other hand at 77 K there is only about a 4% increase in the positive coefficient. The net

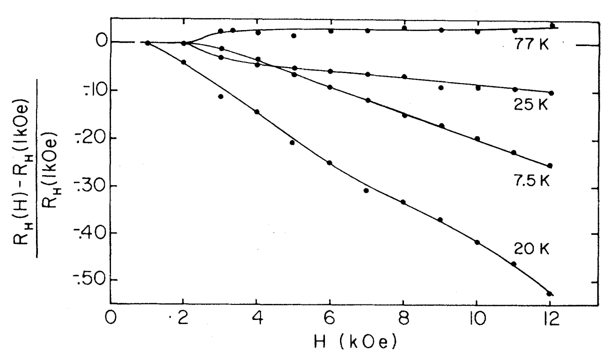

FIG. 4. Fractional change in the Hall coefficient with magnetic field for pure $NbSe_2$ at several different temperatures.

result between 1 and 12 kOe is a shift upward of about 0.5 deg of the temperature where the Hall coefficient changes sign. The field dependence is reduced by the addition of impurities, with small or no effect being observed at higher concentrations. The indication of the data is clear. For pure $NbSe_2$ the CDW transition has been enhanced by the magnetic field.

Recent electron and neutron diffraction studies[1,2] have given strong evidence for CDW formation in transition-metal dichalcogenides. Associated with any CDW must be a periodic lattice distortion of the same period. The change in sign of the Hall coefficient for $NbSe_2$ around 20 K must reflect a changing Fermi-surface geometry induced by the formation of the CDW superlattice which results in a significant change in the number and sign of the carriers. The process in $NbSe_2$ appears to be continuous because of the lack of saturation in the Hall coefficient down to the superconducting transition, indicating a gradual change in the CDW and associated lattice distortion with decreasing temperature. Neutron diffraction studies[2] have indicated a slight decrease in the wavelength of the CDW with decreasing temperature with an associated increase in the amplitude of the wave, i.e., the size of the modulation in the electron density. The introduction of magnetic impurities would appear to have two primary effects—first, a reduction in the temperature for the initial formation of the CDW and second, a limiting of its amplitude.

The formation of CDW's must result from a particular relation between electron-electron and electron-phonon interactions.[6] The introduction of small amounts of impurities has little influence on the electron-phonon interaction. This can be seen in the small effect produced by large concentrations of Al. Therefore, the principal impurity effect must be on the electron-electron interaction.

For the superconducting state, the effect of magnetic impurities seems to be adequately described by an exchange interaction between the impurity spins and the conduction electrons which results in a breaking up of the superconducting pairs.[7] For CDW's, the data indicate that it is again the spin of the impurity which is the influencing factor in the interaction. The observation[4] of a significant Kondo effect in Fe- and Mn-doped $NbSe_2$ indicates that the impurity is in a magnetic state. The exchange between the impurity spins and the conduction electrons must have a destructive influence on the electron-electron spin interaction, possibly in a manner similar to that in the superconducting state. Such an interaction would be expected both to decrease the T_c for CDW formation and to decrease the amplitude of the wave. The most surprising aspect of this interaction is the indication that the impurity-concentration dependence produces almost identical effects in the two systems.

One possible explanation of the increase in T_c for the CDW formation with magnetic field would be a CDW state which is stabilized by an interaction between parallel-spin electrons. The spin alignment by the field would enhance the coupling of parallel spins in the direction of the field and thus tend to increase T_c for CDW formation.

The data presented here, I believe, present significant new information concerning the possible CDW state in $NbSe_2$. The effect of a magnetic field and of atomic impurities on this state offers some of the first information on a possible mechanism for the CDW transition. The similarity between the effects of the magnetic impurities on the CDW and on superconductivity is extremely intriguing. Similar property changes to those observed in $NbSe_2$ have been observed in other superconducting materials such as the *A*15 compounds. The connection between the two states, CDW and superconducting, should offer significant possibilities for future study.

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