Transport properties and magnetic ordering in iron-doped $NbSe_2$

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The resistivity ρ and Hall coefficient R_H are reported for Fe_xNbSe_2 for $0.005 \leq x \leq 0.33$ over the entire temperature range for 1.5 to 300 K. The magnetic state of the iron dramatically affects these transport properties. At low concentrations the transport properties appear to reflect a Kondo-like interaction between the iron moment and the charge carriers. In the intermediate concentration range anomalous behavior in both ρ and R_H is consistent with the iron forming a spin-glass or spin-density-wave state. At still higher concentrations an antiferromagnetic state is indicated. These states are in agreement with susceptibility measurements. Anisotropic behavior in R_H and in the susceptibility and the unusual behavior of the transport properties lead to a model of an anisotropic spin-glass state in which only the spin component perpendicular to the layers is "locked."

I. INTRODUCTION

The layer-structured dichalcogenide compounds intercalated with magnetic ions have shown interesting and unusual behavior in their electrical and magnetic properties. The magnetic susceptibility[1] of Fe_xNbSe_2 for $x \leq 0.05$ shows Curie-Weiss behavior down to $T \approx 1.5$ K. Additional studies[2] have shown sharp susceptibility maxima for magnetic fields perpendicular to the layers in the concentration range $0.08 \leq x \leq 0.18$ with the temperature of the maximum increasing monotonically with Fe concentration. This behavior has been shown to be qualitatively similar to that observed in spin-glasses[2] but is also consistent with a spin-density-wave mechanism.[3] At concentrations above $x = 0.20$ the susceptibility maximum moves to a higher-temperature range and is characteristic of an antiferromagnetic transition which has been previously observed.[4]

The magnetic susceptibility of $2H$-Fe_xTaSe_2 and $4Hb$-Fe_xTaS_2 for $x \leq 0.10$ show similar maxima to $2H$-Fe_xNbSe_2 although at slightly lower concentrations and in addition have positive Weiss constants[1] above $x = 0.08$, in contrast to the negative ones observed for Fe_xNbSe_2 over the entire iron concentration range.[2] Both the Nb and the Ta compounds show substantial anisotropy in the susceptibility.

Previous studies of the transport properties of these Fe intercalated materials have not been extensive, but indicate a significant effect of the magnetic ion on these properties. Fe_xNbSe_2 for $x \leq 0.05$ has a low-temperature-resistivity minimum which moves to higher temperature as the concentration increases. This minimum shows significant and anomalous anisotropic magnetic field effects.[5] A large concentration-dependent increase in the Hall coefficient has been observed at low temperatures[6] which is nonlinear at high magnetic fields.[7] The $2H$-Fe_xTaSe_2 compounds show similar properties.[7]

In this paper we present the results of a study of the electrical transport properties of single-crystal $2H$-$NbSe_2$ intercalated with iron concentrations up to 33 at.% over the entire temperature range from 1.5 to 300 K. These studies have centered on the concentration and temperature dependence of the resistivity and Hall coefficients and show that at low temperatures these transport properties are strongly influenced by the presence of the magnetic ion over the entire iron concentration range. Examination of these transport properties yields additional information concerning the magnetic state of the iron.

II. EXPERIMENTAL TECHNIQUES

Single crystals of Fe_xNbSe_2 were grown from the powdered compound which had been made by heating the appropriate amounts of the elements in sealed, evacuated quartz tubes at 750 °C for four days. The single crystals were then grown by an iodine-vapor transport technique[8] using a 800-600-800 °C gradient and about a 5-d growing period. Hexagonal platelets with good shiny surfaces were obtained at all concentrations below $x = 0.33$. The $x = 0.33$ samples show some surface irregularities. At the lower Fe concentrations crystals larger than 1 cm^2 could be produced where at the higher concentrations only crystals about one-quarter this size could be obtained.

Iron concentrations were checked using x-ray-fluorescence analysis. Although no absolute values for the Fe concentration could be measured because of the lack of standards and the effects of self-absorption by the crystals during fluorescence, the measured Fe concentrations do increase approximately linearly with the nominal concentration and these

values are used in reporting the data in this paper.

Resistivity measurements were made using standard four-lead techniques on rectangular bars cut from the grown crystals. Typical sample dimensions were 3.5–5.0-mm length, 0.2–0.3-mm width, and 0.01–0.03-mm thickness. Exact cross-sectional areas were calculated from measured sample masses and lengths along with densities calculated from the measured lattice parameters of $NbSe_2$. Using this method, absolute resistivities could be determined to an accuracy of 5–10%. Almost the entire error is due to the uncertainty in the measured distance between voltage contacts on the crystals since these were made with silver-conducting paint which had a rather large area of contact. Current densities of 30–150 A/cm^2 were used, with all currents being parallel to the crystal layers.

Samples used for Hall-coefficient measurements were similar to the resistivity samples except for greater widths. Hall voltages were measured for two different magnetic field crystal configurations. The "parallel" configuration measured the Hall voltage in the plane of the layers with the field perpendicular to the layers. The "perpendicular" configuration measured the Hall voltage perpendicular to the layers with the field in the plane of the layers. The current was always in the plane of the layers. Absolute values of the Hall coefficient for the parallel configurations are good to about ±4% where as in the perpendicular case they are only good to approximately ±20% due mainly to the necessity of measuring much smaller voltages.

Room-temperature x-ray powder-diffraction measurements were made to check the crystal structure and phase of the Fe_xNbSe_2 crystals. The crystals were ground into powders and measurements were made with a standard film camera. The measurements confirm the $2H$ structure for all Fe concentrations. Although high-precision measurements of the lattice parameters could not be made, there is no indication of any significant change in the room-temperature lattice constants even at the highest Fe concentrations. Also no additional lines are observed for $x \leq 0.20$ and relative line intensities for the higher concentrations are very similar, although not identical, to those of the lowest concentrations. Thus, there is no indication at room temperature of any significant change in the crystal structure even at large concentrations of Fe and below $x = 0.20$ no indication of any ordering or clumping of the iron.

III. EXPERIMENTAL RESULTS

A. Resistivity

Resistivity measurements were made on Fe_xNbSe_2 for $0.005 \leq x \leq 0.33$ and the results for 5 K ≤ temperature ≤300 K are shown in Fig. 1. At room temperature the resistivity increases with increasing x with ρ closely proportional to $x^{0.30}$ above $x = 0.02$. At low temperatures the resistivity shows considerable variation with both temperature and iron concentration. The resistivity at 5 K increases at the lower concentrations before reaching a rather sharp maximum near $x = 0.18$ and then decreasing for high concentrations. It is clear from the figure that this low-temperature drop in the resistivity results because of a pronounced change in the slope $(d\rho/dT)$ which occurs at a fairly well defined temperature.

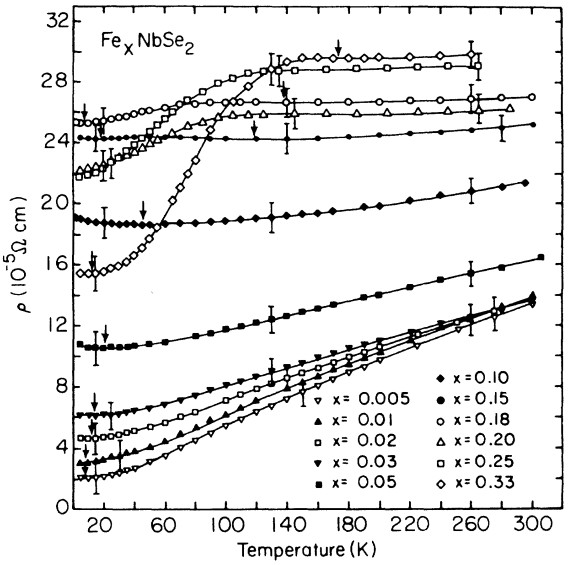

FIG. 1. Resistivity ρ as a function of temperature of Fe_xNbSe_2 for $0.005 \leq x \leq 0.33$. Arrows indicate the position of relative minima.

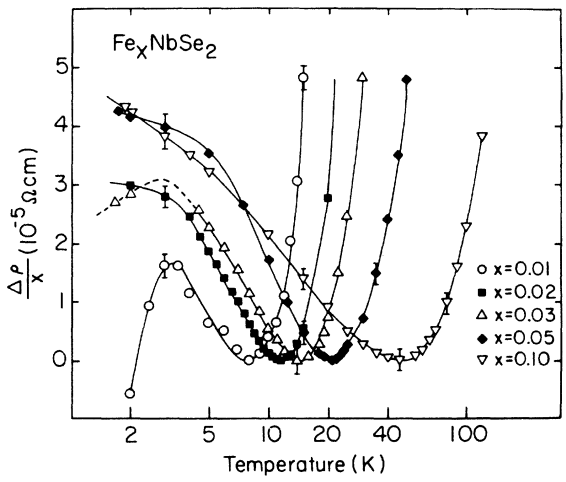

FIG. 2. The ratio $\Delta\rho/x$, where $\Delta\rho = \rho(T) - \rho(T_{min})$, as a function of $\log_{10}T$ for Fe_xNbSe_2 with $0.01 \leq x \leq 0.10$.

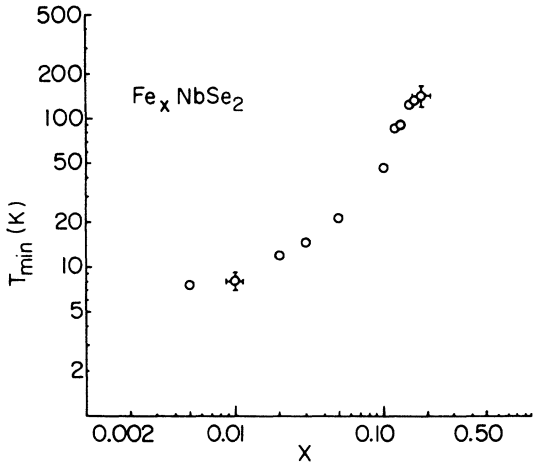

FIG. 3. Log_{10} of temperature of the minimum in the resistivity (T_{min}) vs $\log_{10}x$ for Fe_xNbSe_2.

This break point increases from around 90 K at $x=0.18$ to about 150 K for $x=0.33$ (see Fig. 7).

Shallow minima are observed in many of the resistivity versus temperature curves and these are indicated by the arrows in Fig. 1. An expanded plot of $\rho-\rho_{min}$ normalized to the iron concentration versus $\log_{10}$ temperature for $x\leq 0.10$ is shown in Fig. 2. The $\log_{10}$ T behavior is consistent with previously reported behavior. However, this particular minimum is not confined just to the lowest concentrations but can be traced all the way to $x=0.33$ as seen in Fig. 1 and also in Fig. 3 where the temperature of the minima are plotted versus concentration. There does not appear to be any simple power relationship between T_{min} and x.

A close examination of Fig. 1 shows that for the concentrations $x=0.15$ and 0.18 there are in fact two minima in ρ vs T. This can be seen clearly in Fig. 4. At $x=0.12$ there is an inflection in the ρ vs T curve near 20 K which, as the concentration increases, becomes a relative maximum followed at a lower temperature by a second minimum. At $x=0.18$ (Fig. 1) the magnitude of the resistivity drop has increased in size and by $x=0.20$ represents a significant fractional decrease in the resistivity. The second minimum is not observed for $x=0.20$ and 0.25 but again seems to appear slightly at $x=0.33$. This is also true for the higher-temperature minimum. The temperature of the second minimum decreases from approximately 17.5 K at $x=0.15$ to 7.5 K at $x=0.18$ whereas, the temperature at which ρ starts decreasing increases over the same concentration range (see Fig. 7).

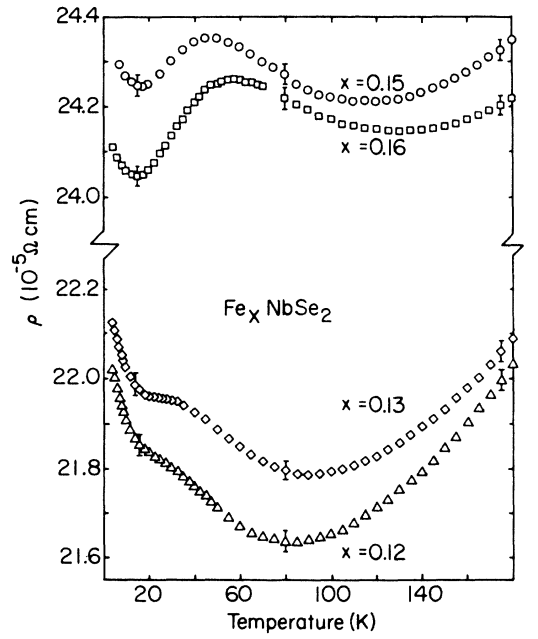

FIG. 4. Resistivity ρ on expanded scale as a function of temperature for Fe_xNbSe_2 in the intermediate Fe concentration range.

B. Hall coefficient

The temperature dependence of the "parallel" Hall coefficient (R_H) of Fe_xNbSe_2 for $0\leq x\leq 0.33$ is shown in Figs. 5 and 6. Within the uncertainty, all

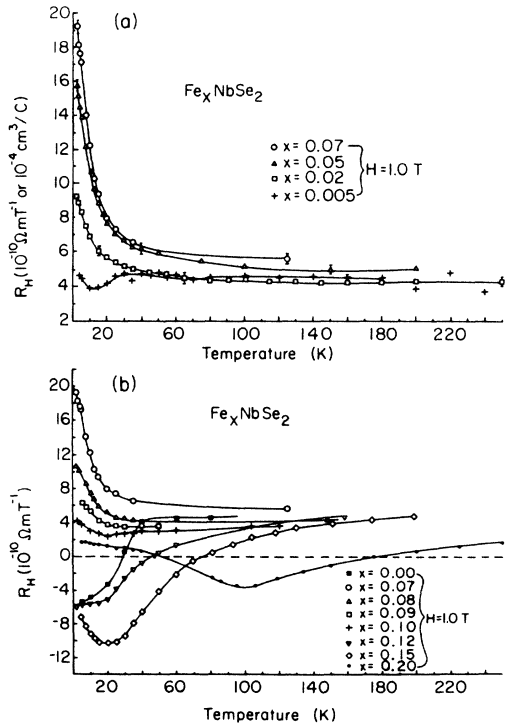

FIG. 5. Parallel Hall coefficient (R_H) as a function of temperature for Fe_xNbSe_2. (a) $x\leq 0.07$. (b) $0.07\leq x\leq 0.20$. R_H for pure $NbSe_2$ is also shown.

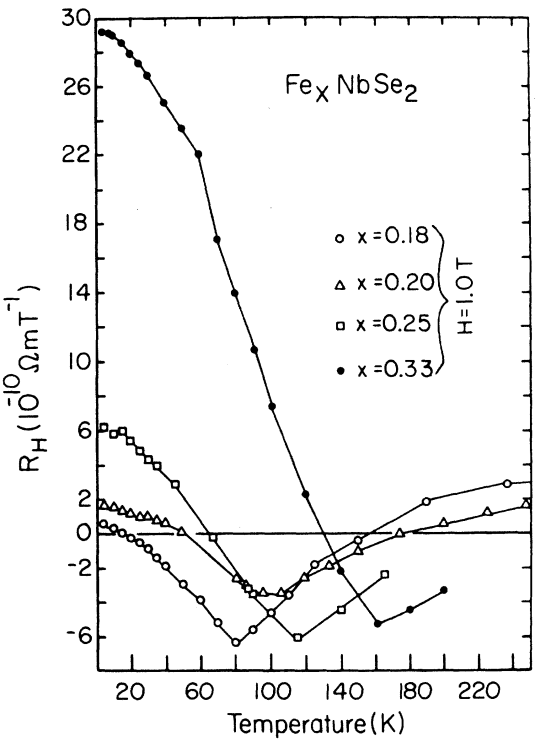

FIG. 6. Parallel Hall coefficient (R_H) as a function of temperature for Fe_xNbSe_2 with $0.18 \leq x \leq 0.33$.

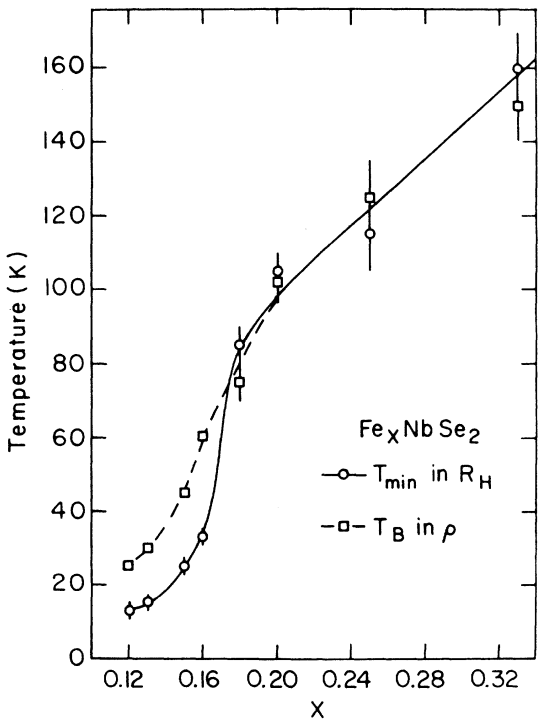

FIG. 7. Temperature of the minima in R_H and the temperature of the sharp down turn in ρ, T_B, as a function of x for Fe_xNbSe_2.

concentrations except the two highest show the same room-temperature R_H of approximately $+4.5 \times 10^{-10}$ volt m/(Amp T) or $+4.5 \times 10^{-4}$ cm^3/C. At low temperatures the first effect observed for the lowest concentrations of iron is the disappearance of the change in sign of R_H around 30 K observed in pure $NbSe_2$, which is believed to result from the formation of a charge-density wave. This effect has been previously reported[6] and can be seen by comparing the $x = 0.005$ data of Fig. 5(a) to the $x = 0$ data of Fig. 5(b). For $0.005 \leq x \leq 0.07$, R_H shows a low-temperature increase which is proportional to x as seen in Fig. 5(a). These results agree with previous measurements in this concentration range.[6,7] Above $x = 0.07$ however, the low-temperature increase becomes smaller with increasing concentration. Similar behavior of R_H at 4.2 K has been reported[1] for Fe_xTaSe_2. This trend continues until $x = 0.10$ above which R_H no longer increases but begins to decrease at low temperature as shown in Fig. 5(b). For $x = 0.12$ a change in sign is observed and for concentrations above $x = 0.13$, a negative minimum in R_H occurs. At high concentrations (Fig. 6) R_H continues to show the negative minimum but this is followed at a lower temperature by a sign change back to a positive value at the lowest temperatures. The temperature at which the minimum in R_H occurs increases with increasing x as shown in Fig. 7.

In the intermediate concentration range $0.11 \leq x \leq 0.18$, R_H versus temperature shows considerable magnetic-field dependence in the region of the minimum as can be seen in Fig. 8 where data at 1.0 and 0.2 T are compared. The primary effect observed is that the higher field washes out the minimum in R_H. For $x = 0.12$ and 0.13 no minima are observed at 1.0 T—just a flattening of R_H versus temperature—but at 0.2 T definite minima exist. For higher concentrations the sharp minima at 0.2 T become shallower and rather rounded at 1.0 T. For the $x = 0.15$ sample, R_H at 20 K decreases with field up to 4 T with no minimum observed at the highest fields. For Fe concentrations above those of Fig. 8 little or no field dependence of R_H is observed up to 1.2 T.

The perpendicular Hall coefficient ($R_{H\perp}$) is of the same magnitude as the parallel coefficient but shows very different behavior as a function of concentration as seen in Fig. 9. For $x \leq 0.07$ the room-temperature values of $R_{H\perp}$ converge to approximately the same value ($\approx 4 \times 10^{-10}$ Ω m/T or about the same as R_H). At higher concentrations the trend is to smaller, perhaps even slightly negative, values. At low temperatures $R_{H\perp}$ decreases from positive to negative values as x increases up to $x = 0.12$ and then remains

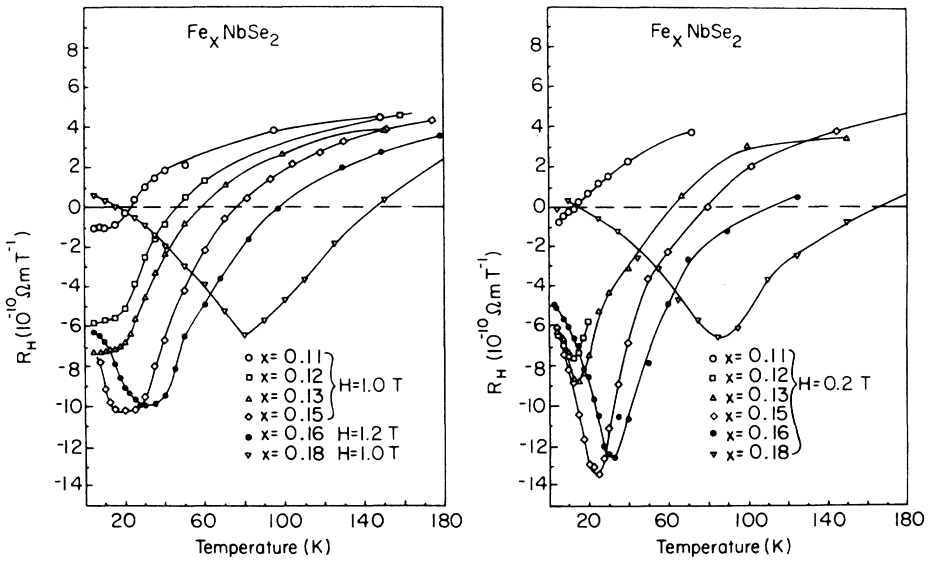

FIG. 8. Parallel Hall coefficient (R_H) as a function of temperature for Fe_xNbSe_2 in the intermediate concentration range $0.11 \leq x \leq 0.18$. (a) $H = 1.0$ or 1.2 T. (b) Same samples as (a) but $H = 0.2$ T.

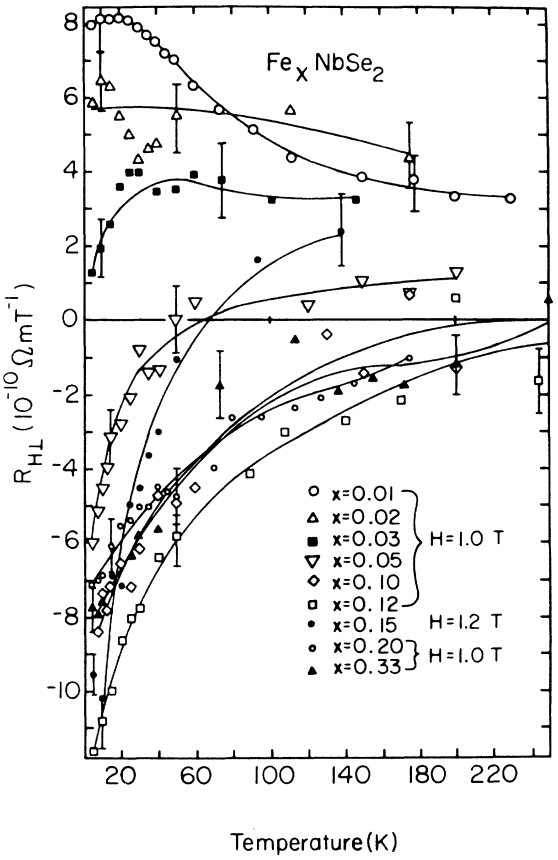

FIG. 9. Perpendicular Hall coefficient $R_{H\perp}$ as a function of temperature for Fe_xNbSe_2 with $0.01 \leq x \leq 0.33$.

approximately constant, within experimental error, for higher concentrations. As mentioned previously, the error in these data are significant (20%), which makes it difficult to observe any fine structure; however, it seems clear that $R_{H\perp}$ is not being affected as significantly by the magnetic state of the iron as R_H or the resistivity.

IV. DISCUSSION

The relatively small effects that the Fe has on the transport properties of Fe_xNbSe_2 at room temperature (an increase in ρ by a factor of 2.5 and little change in the Hall coefficient until the highest concentrations) indicate that the valence electrons of the iron must be involved only in bonding and are not contributed to the niobium $4d$ band which is believed to be[9] the conduction band in $NbSe_2$. Recent optical studies support this contention.[10] This would then dictate that the effects observed at low temperatures must reflect the direct interaction between the magnetic moment of the Fe and the charge carriers.

The scattering of conduction electrons from magnetic impurities can be dealt with in the framework of The *sd*-exchange interaction.[11] Within this model, Kondo[12] has shown that inelastic spin-flip scattering can result in a $\log_{10}T$ increase in the resistivity at low temperatures such as observed in many dilute magnetic impurity systems. Magnetic fields as well as spin-spin interactions inhibit such spin-flip scattering and thus reduce the resistivity due to this scattering.

In the Hall coefficient the normal Lorentz force is modified because the scattering probabilities of the

spin-up and spin-down itinerant electrons are different in an applied field. The relaxation times for the two spin directions display a characteristic $\log_{10}T$ behavior which Suhl[13] has shown can lead to an increasing Hall coefficient at low temperatures when an energy averaging of the up- and down-spin electron lifetimes is performed. Within this model Béal-Monod and Weiner[14] show that there should be a low-field H^2 increase of R_H which comes from the magnetization of the impurity spins and a high-field $\log_{10}H$ decrease[15] once the impurity spin is saturated.

A second scattering mechanism which can produce an anomalous or extraordinary component of the Hall coefficient is the so-called skew scattering which results in a left-right asymmetry in the scattering with respect to the plane formed by the impurity moment and the incident velocity of the electron.[16] This arises from the spin-orbit coupling between the electron's angular momentum and the impurity's magnetic moment during the electron's residence in the impurity's virtual state. The magnitude of this contribution for a system whose susceptibility obeys the Curie law would be given by

$$R_H = R_{H0} + AnT^{-1} \quad , \tag{1}$$

where R_{H0} is the nonskew-scattering component of the Hall coefficient, n the impurity concentration, T the temperature, and A the parameter describing the strength of the scattering.[17] Unfortunately all systems do not seem strictly to obey this relationship. Experimentally the skew component of R_H is largest at the lowest fields and decreases to a saturation value at high fields.[18]

At the lowest Fe concentrations (up to $x=0.07$), the behavior of both the resistivity and Hall coefficient of Fe_xNbSe_2 is generally consistent with that expected with from a Kondo interaction. Such an explanation has been previously proposed with the additional evidence of negative magnetoresistance behavior, particularly for fields perpendicular to the layers,[5] and of a $\log H$ decrease in the Hall coefficient[7] at high fields giving further support to this contention. Fig. 2 is also supportive of this idea since over a short range below the minimum the resistivities show the $\log_{10}T$ increases which have parallel slopes when normalized to the Fe concentration as predicted by the Kondo theory. These data are in contrast to previously published results[7] which did not show paralled slopes for concentrations below 0.05.

There are, however, several large inconsistencies which exist with the Kondo model. As Fig. 3 shows, the resistivity minimum persists far beyond what could be called a dilute concentration of iron into a region where spin-spin interactions should be strong. Also at $x=0.07$ the Hall coefficient shows a definite change in character which also could indicate the beginning of an interaction between the Fe moments. Such an interaction—be it direct spin-spin or Ruderman-Kittel-Kasuya-Yosida (RKKY)—has been confirmed by susceptibility measurements.[2] Thus there is strong evidence for a spin-spin interaction which should wipe out Kondo scattering (and thus the resistivity minimum), or at least possibly result in a low-temperature relative maximum in the resisitivity.[19] Neither of these effects is observed. In addition the Hall coefficient does not show a low-field increase as theory would predict, but rather we have confirmed that the $\log_{10}H$ decrease observed in R_H at high fields[7] in fact is observed down to fields as low as 0.1 T. Also, as far as we can determine, the variation in the Hall coefficient with temperature is much larger than observed in any other system which exhibits a spin contribution to the Hall coefficient.[20] All of this suggests that Fe_xNbSe_2 is probably not a conventional Kondo system even at lower concentrations.

The concentration dependence of the resistivity minimum (Fig. 3) does not follows any particular power of x but rather shows a more rapid increase with x as the iron concentration is increased. This would be expected even if the additional Kondo-like resistivity at low temperatures does have a unique concentration dependence since at high temperatures $d\rho/dT$ for $NbSe_2$ is significantly smaller than at low temperatures which would result in a more rapid rise in the temperature of the minimum with concentration.

Now it is in the intermediate concentration range ($0.10 \leq x \leq 0.18$) that both the resistivity and the parallel Hall coefficient show the most intriguing behavior. It was previously proposed[21] that the behavior in this concentration region was suggestive of a spin-glass state and subsequent susceptibility studies[1,2] give strong support for such a state. However, Antoniou[3] have examined the Fe-doped layer structures in a model of an impurity-induced spin-density wave (SDW) in the background of a smeared charge-density wave. His model is also consistent with the susceptibility measurements on both $2H$-Fe_xTaSe_2 and $2H$-Fe_xNbSe_2 such that susceptibility studies are not definitive in resolving which of these models is correct. In either case the sharp step observed here in the resistivity would result from a decrease in the spin-flip scattering due to the "locking in" of the spins in the spin-glass or the ordering in the SDW. However, we are not aware of any spin-glass system where the transition results in such a drop in the resistivity. In order to examine the $\Delta\rho$ associated with iron, Fig. 10 shows the resistivity data of Fig. 1 with the resistivity of $Fe_{0.005}NbSe_2$ subtracted from it. In a typical spin-glass, $\Delta\rho$ should show a low-temperature maximum followed at lower temperatures by a linear region and at still lower temperatures by $T^{3/2}$ dependence.[22] This maximum

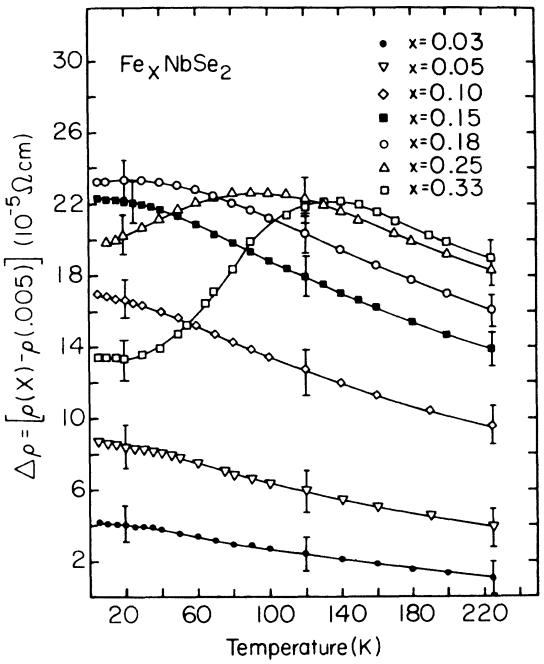

FIG. 10. The temperature dependence of the charge in the resistivity $\Delta\rho$ due to iron obtained by subtracting the resistivity of $Fe_{0.005}NbSe_2$ from the resistivity for other iron concentrations. No maxima are observed in the spin-glass concentration region.

comes about because the locking in of the spins. Figure 10 demonstrates that no maximum is observed for any intermediate concentration. This would seem to indicate that if a spin-glass is formed it is not quenching as much of the magnetic scattering as in a typical spin-glass system.

Antoniou[3] has tried to explain the relative maximum in the resistivity which is observed in some Fe_xTaSe_2 and Fe_xNbSe_2 samples below the minimum as due to quenching of the spin-flip scattering by the formation of a SDW. However, a close examination of Fig. 4 shows that the drop in the resistivity observed here is not a quenching of the rising resistivity below the minimum but is in fact superimposed on it. Below the drop the resistivity is again seen to rise with approximately the same slope as above it thus resulting in a second minimum. From this it would appear that although the resistivity drop observed for Fe_xNbSe_2 probably does reflect a quenching of some spin-flip scattering, it is not that scattering which produces the Kondo-like behavior. The small size of the drop is resistivity in this concentration range would seem to indicate that only a small fraction of the magnetic scattering is being quenched. Although the reason for this behavior is not clear, it could reflect a spin-glass state in which only a certain component or components of the spin are locked in or possibly a nonuniform distribution of the iron where only small regions reach the critical concentration necessary for spin-glass or SDW formation.

Behavior similar to that observed in the Hall coefficient of Fe_xNbSe_2 for $0.11 \leq x \leq 0.18$ has been seen for reasonably dilute alloys of transition-metal ions in the noble metals[23] with the general temperature dependence of the Hall coefficient being ascribed to skew scattering. The minimum in R_H occurs when the localized moments are "frozen" into a spin-glass state and a field dependence of the minimum is observed which is similar to that shown by Fe_xNbSe_2. In order to compare the Hall coefficient of Fe_xNbSe_2 in the intermediate concentration range to that predicted by skew scattering, R_H is plotted versus T^{-1} in Fig. 11. [See Eq. (1).] At high temperatures there is an approximate linear dependence, with this dependence particularly evident at the higher concentrations. At high fields (up to 4 T) R_H decreases with increasing field which is also consistent with the behavior of spin-glass noble-metal system.[18] However, the Fe_xNbSe_2 system shows a much weaker dependence on magnetic field of the minimum in R_H than shown[23] by either Au–Fe or Au–Mn. This would indicate that in Fe_xNbSe_2 the field must be a smaller perturbation on the RKKY coupling.[22] It appears that a skew-scattering mechanism can give a reasonable description of the behavior of R_H in this concentration range. If an SDW were formed it

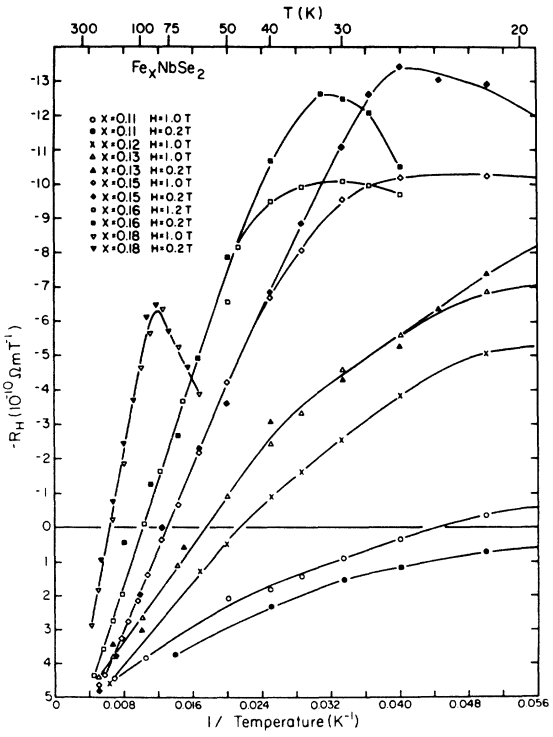

FIG. 11. The negative of the parallel Hall coefficient R_H as a function of the inverse temperature for iron concentrations in the intermediate range.

would also result in a decrease of the spins capable of being aligned by the field.

The drop in resistivity occurs at a higher temperature than the minimum in R_H as seen in Fig. 7. In fact it appears that the minimum in R_H more closely corresponds to the second minimum in the resistivity. In the spin-glass model this would indicate that the spin-flip scattering is quenched before the transition actually occurs which does not seem unreasonable.

Although it is not clear why the primary contribution to the Hall coefficient changes from what appears to be a positive Kondo-spin-flip scattering component at low concentrations to a negative skew-scattering component at intermediate concentrations, some comments can be made. It would seem reasonable to believe that at the low concentrations both mechanisms are active, but the spin-flip scattering dominates. This scattering should to a great extent be quenched by the impurity spin-spin interaction which would allow the skew scattering to dominate at higher concentrations. Now Eq. (1) predicts that the slopes of the curves in Fig. 11 should be proportional to the iron concentration in the ideal skew-scattering case, however the slopes increase much more rapidly than the iron concentration which would imply that its scattering strength is enhanced by the impurity spin-spin interaction. Such an enhancement is difficult to understand since the spin-spin coupling is antiferromagnetic, as indicated by the susceptibility,[2] which would tend to reduce the skew-scattering strength. The resolution of the problem is not yet apparent.

The transport properties of Fe_xNbSe_2 show significant changes in behavior near $x=0.20$ which appear consistent with a change to an antiferromagnetic state as seen in the susceptibility studies.[2] (See Figs. 2 and 8.) The sharp decrease in resistivity at low temperatures is consistent with the reduction of both the spin-flip and nonspin-flip scattering as expected below the Néel temperature in an antiferromagnet. A similar decrease in the resistivity was observed by Friend *et al.*[24] in $Fe_{0.33}NbS_2$ at the antiferromagnetic transition. They also speculate, based on the behavior of the Hall coefficient, a new magnetic superlattice below the Néel temperature which introduces gaps in the energy spectrum at the new Brillouin-zone boundaries and thus reduces the number of carriers. Although the behavior of the Hall coefficient in $Fe_{0.33}NbSe_2$ differs some from that of $Fe_{0.33}NbS_2$, it is certainly possible that a similar periodicity change and reduction in carriers could occur along with a decrease in magnetic scattering.

The Hall coefficient at high concentrations appears to continue to display skew-scattering behavior and the resulting minimum when the magnetic ordering occurs (see Fig. 6), but not the field dependence observed for the intermediate concentration range. For $x=0.33$ exceptionally large, positive values of R_H—much larger than the room-temperature value—are observed at the low temperatures. Below the magnetic-ordering temperature the skew scattering should be reduced, and it is difficult to see another spin-scattering mechanism in the antiferromagnetic state which could make such a contribution to R_H; therefore, it appears reasonable to conclude, as Friend *et al.*[24] did for $Fe_{0.33}NbS_2$, that a new magnetic superlattice is formed with the subsequent reduction in carriers which just results in an enhanced ordinary Lorentz contribution to the Hall coefficient.

The perpendicular Hall coefficient (field parallel to layers, voltage perpendicualr to layers) shows no sign of the positive increase in $R_{H\perp}$ observed in the parallel case at low concentrations nor any changes which can be associated with magnetic ordering (Fig. 9). In the measurements of Hillenius and Coleman[2] the susceptibility is also anisotropic showing little or no sign of magnetic ordering for fields parallel to the layers in the intermediate concentration range and significant anisotropy in the high concentration range where the antiferromagnetic transition is observed. Thus both the Hall measurements and the susceptibility would seem to indicate that for fields parallel to the layers there is no spin-glass or SDW ordering.

This means in the spin-glass model that the moments would lock in only with respect to alignment perpendicular to the layers and not parallel to the layers thus forming an anisotropic spin-glass in which the "ordering" is only along one axis. Recently Atzmony *et al.*[25] have reported anisotropic spin-glass behavior in the insulator Fe_2TiO_5, but we believe that this is the first time such behavior has been proposed for a metallic system. The magnetoresistance for the low concentration, Kondo-like systems, which is small for perpendicular fields but large enough for parallel fields to "wipe out" the resistivity minimum,[5] can be explained in such a model if one assumes that it is Kondo spin-flip scattering of the spin components lying in the plane of the layers that is largely responsible for the effects with little contribution from spin components perpendicular to the layers. This "one-directional spin locking" could also explain the simultaneous observation of a Kondo-like resistivity behavior and magnetic ordering. The low-concentration, positive contribution to R_H appears to recede when the spins begin to interact and quench the spin-flip scattering of the spin components perpendicular to the layers. The skew scattering which then dominates is itself quenched when the spin-glass ordering perpendicular to the layers no longer allows free alignment of the spins in this direction. The spin-flip resistive scattering would also be quenched as manifest in the small resistive drop observed. The spin components in the plane of the layers would remain "free," however, resulting in a simultaneous Kondo-like behavior (see Fig. 4). It is not clear if the SDW model of the spin ordering could also ex-

plain the anisotropic behavior in the transport and magnetic properties, but is conceivable that an SDW could also have anisotropic character.

At the highest concentrations it appears that all spin components must order since the susceptibility shows antiferromagnetic behavior for fields both perpendicular and parallel to the layers,[2] and the resistivity shows large decreases; however, no indication of this is observed in the perpendicular Hall coefficient.

V. CONCLUSIONS

A detailed study of the resistivity and Hall coefficient for Fe_xNbSe_2 for $0.005 \leq x \leq 0.33$ has revealed distinctive effects of the magnetic state of the iron on these transport properties and has helped to characterize the magnetic state. For Fe concentrations $x \leq 0.07$ both the resistivity and Hall coefficients show behavior which is generally consistent with the Fe being in a dilute state in which the carrier scattering can be described by the Kondo-like interaction. There are, however, some aspects of the behavior which are unusual or in disagreement with theory, namely, the large temperature dependence of R_H, its behavior at low fields and, most importantly, the observation of a resistivity minimum far beyond what could be called dilute concentrations.

In the intermediate concentration range of $0.11 \leq x \leq 0.18$ the Hall coefficient appears to be dominated by a skew-scattering component whose quenching by a spin-glass or SDW transition results in a minimum in R_H which shows large magnetic-field dependence. These transport measurements are not able to differentiate between the two models for the magnetic ordering. At this magnetic transition the resistivity exhibits a small drop which is consistent with a magnetic ordering but, as far as we have been able to find, has not previously been seen in spin-glass systems.

At the highest Fe concentration $0.20 \leq x \leq 0.33$ the resistivity exhibits behavior which is consistent with the antiferromagnetic state observed in the susceptibility.[2] The Hall coefficient continues to show skew-scattering behavior above the magnetic-ordering temperature, while below this temperature its behavior is not completely understood but may reflect formation of a magnetic superlattice and a subsequent reduction in carriers.

The perpendicular Hall coefficeint shows very anisotropic behavior compared to the parallel coefficient and no indication of magnetic ordering. This coupled with all the other anisotropy properties leads to a proposed model in which spin-glass ordering occurs only with respect to the axis perpendicular to the layers with no ordering in the plane of the layers. We know of no other case where an anisotropic spin-glass has been proposed for a metallic system which makes this model unique; however, it does appear to explain most aspects of the transport and susceptibility data.[2]

The Fe_xNbSe_2 compounds have proved to be a truly interesting system in that the transport properties show such strong effects of the iron's magnetic state. Further observations, both experimental and theoretical, are necessary in order to understand completely the anisotropic character of these magnetic states and their interaction with the transport properties.

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