Correlated magnetic and transport properties in the charge-density-wave states of VSe_2

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(Received 7 March 1978; revised manuscript received 26 October 1978)

We report observations of magnetic, transport, and NMR properties in the charge-density-wave (CDW) states of VSe_2. Both the ^{51}V Knight shift and the Hall constant are proportional to the *intrinsic* temperature-dependent magnetic susceptibility of VSe_2, with distinct breaks in behavior at the incommensurate-commensurate transition. We use these relationships to determine the CDW transition temperatures, and to describe physical properties that should guide future theoretical descriptions of CDW's.

I. INTRODUCTION

Charge-density-wave (CDW) systems exhibit a close relationship between structural changes and the associated modifications of electronic character, as reflected in the transport and magnetic properties and superconducting transition temperatures.[1] The role of the Fermi surface in causing CDW's and modifying the electronic properties is understood in general terms,[2] and considerable recent work has addressed the nature of these transitions.[3] But the development and testing of a detailed microscopic theory requires quantitative data on the various physical parameters in the CDW states. In the present note, we report a series of observations made in the CDW states of the layered compound VSe_2. Changes in transport, magnetic, and NMR parameters accompany two CDW transitions in VSe_2 (Ref. 4). Further, strikingly simple, unexpected *correlations* between these properties emerge which should prove useful in extending current theoretical treatments.

VSe_2 is a particularly appropriate candidate for magnetic-resonance study because both the ^{51}V and ^{77}Se nuclei are observable by NMR techniques, providing microscopic probes to complement *macroscopic* observations of the magnetic susceptibility (χ), resistivity (ρ), and Hall constant (R_H). VSe_2 is also an interesting exception to the rules. It is the only layered compound with the metal atom octahedrally coordinated by its neighbors that also possesses a low-temperature continuous CDW transition.[5] In this respect it resembles materials, like $NbSe_2$, in which the metal atom is in a trigonal prismatic environment.

II. EXPERIMENTAL

Transport measurements, ρ and R_H, were performed on single crystals using five contact Van der Pauw[6] and two frequency Hall[7] measurements. The Knight shifts $K(^{51}V)$, $K(^{77}Se)$ with respect to NH_4VO_3 and $(NH_4)_2SeO_4$ standard solutions, were measured using a Varian WL-112 NMR spectrometer. A Foner magnetometer (manufactured by Princeton Applied Research Corp.) was used to measure χ between 2 and 300 K in fields from 1 to 70 kG.

In examining the macroscopic parameters, we begin with the temperature dependence of the transport properties, ρ, and R_H, as shown in Fig. 1. The Hall constant is negative and increases by more than order of magnitude at low temperatures. The resisitivity decreases with temperature, with an inflection occurring in the vicinity of 70 K. Such resistivity behavior is often the signature of the onset of CDW's; very similar variations are observed in $2H$- TaS_2.[1] The present results parallel reports by previous workers,[8-10] although we observe differences in specific details (especially the magnitudes of χ, ρ, and R_H) which will be discussed below. Below 40 K, we find $\rho - \rho_0 \propto T^2$ as also noted in Ref. 8 and similar in behavior to that seen in TiS_2.[11] The magnetic susceptibility data, shown in Fig. 2 for a 2% metal-rich VSe_2 sample, shows that excess vanadium atoms possess localized moments with contributions to χ comparable to that of the VSe_2 layers. The susceptibility maximum, occurring around 110 K, has previously been suggested to reflect the onset of the incommensurate CDW.[8,9] However, our studies of the variation of magnetic susceptibility with vanadium excess suggest that this peak is really an artifact: a combination of increasing χ (as T is lowered) from the paramagnetic excess vanadium species and decreasing χ from the VSe_2 itself.[12]

To isolate the intrinsic contribution to χ from the VSe_2 layers (which we call χ_I), we have examined a suite of VSe_2 samples with varying vanadium excess, fitting the total χ with an expression of the form $\chi = \chi_0 + C/T + \chi_I$. Since this has been discussed at

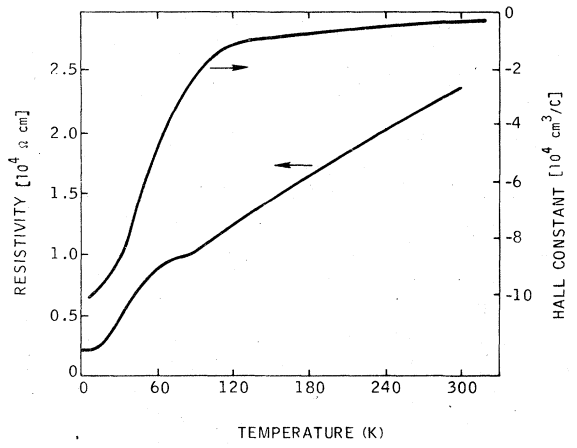

FIG. 1. Temperature dependence of the Hall constant and electrical resistivity of VSe_2.

length elsewhere,[12] the details will not repeated here. However, several consequences of the analysis support the validity of the decomposition procedure. First, the value of the effective moment of the localized vanadium species inferred from the magnitude of C and the known number of excess atoms is $\sim 2.5\mu_B$, the same as values previously observed in the related V_5Se_8 system.[13] Second, the magnitude of the temperature-independent χ_0 associated with the localized moments is consistent with previous observations on localized vanadium species. Finally, as discussed below, the χ_I intrinsic to VSe_2 shows the expected linear correlation with the microscopic susceptibility as reflected in the NMR Knight shift. The resulting χ_I is shown in Fig. 3.

Since previous reports of the transport and magnetic properties have appeared, it is appropriate to compare those data with the present results. The magnetic susceptibility data are to be compared to those of Ref. 10 where data with a negligible paramagnetic tail are reported. The temperature dependent portion of χ_I is the only important contribution to χ_{total} we will consider for purposes of comparison to other temperature-dependent measurements such as the Knight shift. Comparison to Ref. 10 shows that the temperature-dependent terms are similar with a change in χ between 300 and 20 K of 1.7×10^{-4} emu/mole for our data and 1.3×10^{-4} emu/mole from Ref. 10. The greatest difference between our data and those reported by others lies in the temperature-independent contribution. In our deconvolution we find that $\chi_I(T)$ crosses zero. This result contradicts the data of Ref. 10. But, we point out that in the data of Ref. 10 we have no way of detecting a temperature-independent but composition-dependent contribution to χ_{total} while our deconvolution procedure cannot unambiguously separate temperature-independent terms. In light of this ambiguity, we do not assign great significance to the zero crossing but return to it for discussion when comparisons are made to the Hall constant and the Knight shift.

The resistivity and Hall constant data are to be compared to Refs. 8–10. All four sets of data show qualitatively similar features but there are important variations in magnitudes. For example, at 4 K we find $R_H = 1.1 \times 10^{-3}$ cm^3/ C while Ref. 8 obtains 2×10^{-3} and Ref. 9 finds 3×10^{-3}. These large variations of a factor of 3 in the Hall constant cannot be attributed to deviations in stoichiometry within a classical single-band model since variations in

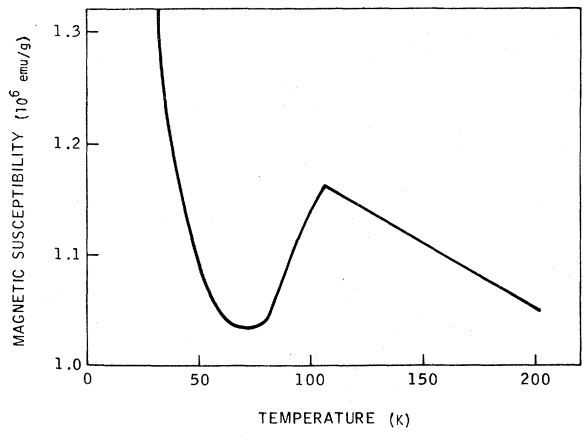

FIG. 2. Temperature dependence of χ for a metal-rich VSe_2 sample (2% excess V), ^{51}V showing the paramagnetic response of the localized moments on the excess vanadium atoms.

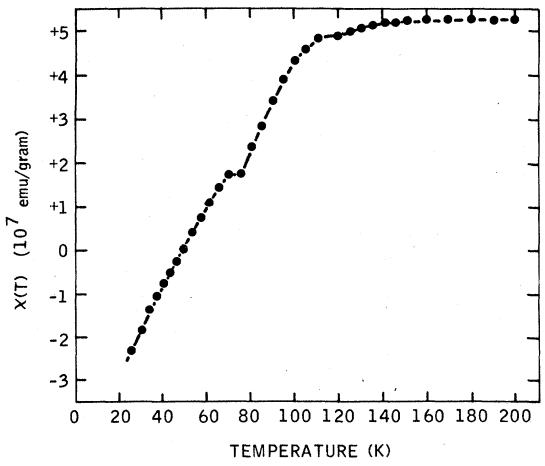

FIG. 3. Susceptibility intrinsic to the VSe_2 layers, $\chi_I(T)$, as determined by the analysis of Ref. 12.

stoichiometry should be less than 5% and only ~30% of the carriers are expected to be involved in the CDW formation. In addition, the temperature-dependent Hall constants are similar for materials with octahedral (VSe_2) and trigonal prismatic ($2H$-TaS_2) coordination at the metal-atom site and are similar for first-, second-, and third-row transition metals (VSe_2, $NbSe_2$, TaS_2).[13] We conclude from these trends and similarities that the transport properties are probably not the result of specific band properties of any one structure type but are rather inherent to electron scattering in the presence of CDW's.

The ^{51}V NMR spectrum of the powdered VSe_2 samples shows a well-articulated series of quadrupolar satellite lines and a central $[\pm\frac{1}{2} \leftrightarrow \mp\frac{1}{2}]$ transition which is broadened by the second-order quadrupole interaction. Assuming an axial field gradient, values of $(e^2qQ/h)^{51}$ of 5.09 and 5.15 MHz are obtained from the first- and second-order broadenings respectively. A change in the electrostatic properties at the vanadium site is seen just below 120 K. As shown in Fig. 4, the derivative of the NMR signal is sharp and the 113 K data are typical of all observations made at higher temperature. A pronounced broadening occurs over a temperature interval of ~15 K with little additional change at lower temperatures. Computer averaging at 13 K showed that the quadrupolar satellites were still present and that the mean splitting was unchanged. However, the derivative signal was roughly an order of magnitude broader, suggesting a distribution in field-gradient values. The Knight shifts of the ^{51}V and ^{77}Se nuclei are shown in Figs. 5 and 6 respectively. Because of the shape changes seen in Fig. 4, the values reported here are determined by finding the center of gravity of the resonance line. Thus these data represent the isotropic Knight shift in each case. The ^{51}V Knight shift is small, negative, and nearly temperature independent at high temperatures ($K(^{51}V) \simeq -0.085\%$). It falls sharply near 120 K and shows a break in slope and a change in sign near 70 K. The ^{77}Se shift also shows a relatively small variation with temperature from 100 to 300 K. A small break in slope is seen near 120 K.

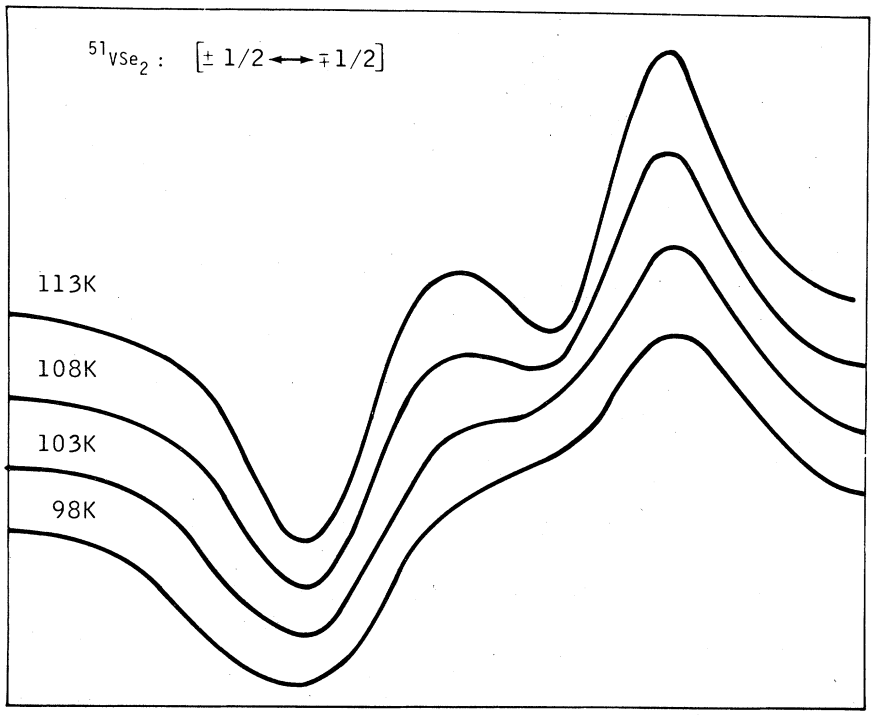

FIG. 4. Broadening of the $[\pm\frac{1}{2} \leftrightarrow -\frac{1}{2}]$ transition of the ^{51}V NMR below 120 K suggests the presence of electrostatic inhomogeneities associated with CDW onset.

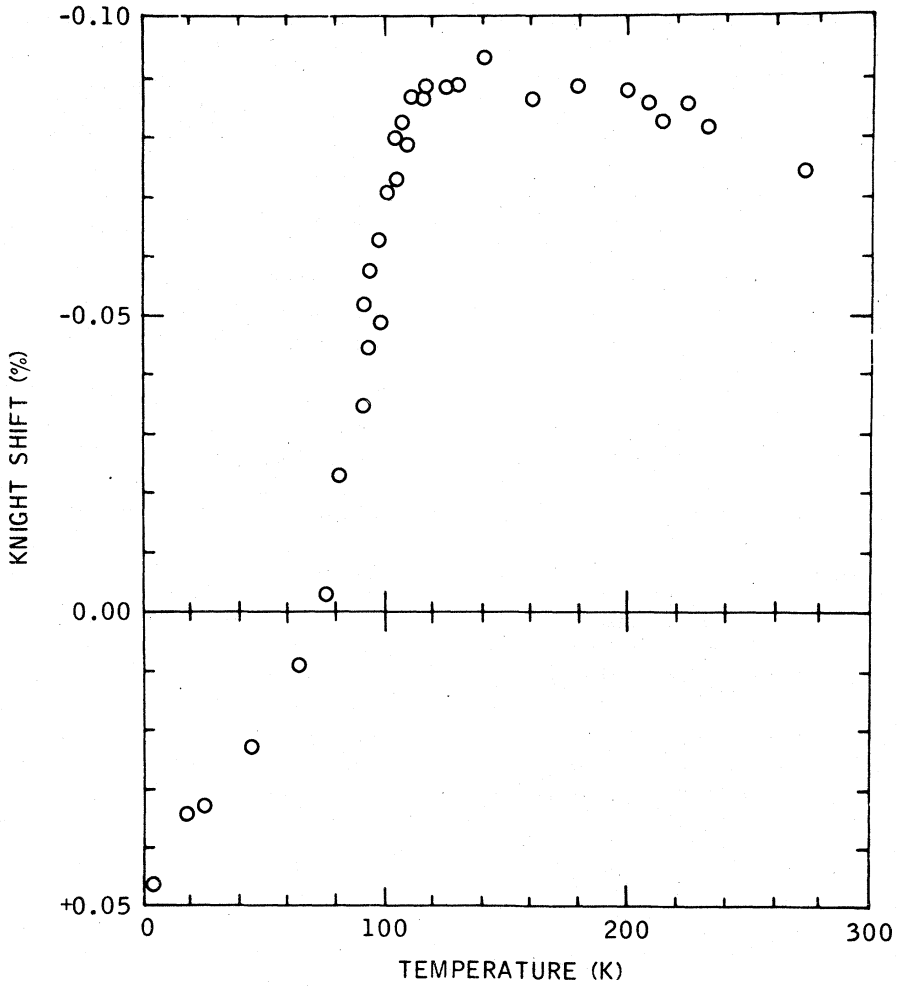

FIG. 5. ^{51}V Knight shift as a function of temperature.

III. DISCUSSION

In attempting to relate these physical properties to the CDW phenomenon we use the data obtained by Williams, *et al.*[14] on one of our samples (with a nominal vanadium excess of 2%). He finds a commensurate CDW superlattice at ~35 K and an incommensurate one at ~100 K. Experimental difficulties precluded him from determining the transition temperature. Knowing the existence of these CDW states, we can review the observations of Sec. II. There is no distinguishing feature in the resistivity data above 100 K which might signal a CDW state. While there are minima and maxima in the $P(T)$ curve at 90 and 70 K respectively, the relationship to CDW transitions is not clear. While R_H begins to increase dramatically near 120 K, there is no obvious additional change in the lower temperature region. As mentioned above, the peak in the total χ does not represent the onset of a CDW state. However, the susceptibility intrinsic to VSe_2, χ_I, does show changes, a small drop near 140 K (of unknown origins), the onset of a large change near 120 K, and a discontinuity near 75 K.

The NMR data provide information related to the CDW states. The broadening of the features of the $[\pm\frac{1}{2} \leftrightarrow \mp\frac{1}{2}]$ transition in VSe_2 in a narrow temperature range below 120 K suggests a change in the electrostatic character of sites which might well be expected with the onset of a CDW. Changes in the Knight shifts of both ^{51}V and ^{77}Se near 120 K also suggest a change in electronic properties. However, on the basis of the low-temperature ^{51}V NMR data seen in Fig. 5, it is hard to deduce any low-temperature transitions. In summary, the nearly continuous variation of the physical parameters in the temperature regime where these CDW transitions occur makes it impossible to determine the transition

temperatures or form a clear picture of the real nature of the electronic changes which are taking place. This is a recurring problem in this class of CDW materials.[1] We will demonstrate that a study of the *correlations* of these parameters, particularly χ, $K(^{51}V)$, and R_H, leads to an unambiguous definition of the transition temperatures and linear relationships between these properties. We believe that this first unambiguous determination of CDW transition temperatures from magnetic and transport data employing the correlation technique can be readily extended to other CDW materials.

Figure 7 shows the correlation between $K(^{51}V)$ and χ_I, plotted with temperature as the implicit variable. Above 120 K, both $K(^{51}V)$ and χ_I are nearly independent of temperature. A linear variation is observed in the incommensurate CDW region, followed by a break in slope at the transition to the commensurate CDW state ($T_d \simeq 70$K). Such linear variations are not necessarily anticipated. The $K(^{51}V)$ and χ_I are related by the hyperfine coupling constants of the conduction electrons and should be proportional for a single-type Fermi-surface electron. Linearity also would be expected for a single Fermi-surface averaged value of the Knight shift, since identical wavefunction averages contribute to both $K(^{51}V)$ and χ.[15] Since the Fermi surface changes as a function of temperature in the CDW transition regions, there is no *a priori* reason for such a simple relationship to hold. This behavior is consistent with the opening of gaps at the Fermi surface: as the CDW amplitude grows, the electronic density of states at the Fermi surface is reduced, but averaging of the Fermi-surface electrons maintains a single-valued Knight shift. The discontinuity in slope at $T_d \sim 70$ K is consistent with the reconstruction of the Fermi surface accompanying the change in metal-atom site symmetry in the commensurate CDW state. The simple proportionality of $K(^{51}V)$ and χ_I supports the deconvolution procedure used to extract χ_I from the total susceptibility.[12] Also note that both $K(^{51}V)$ and χ_I change sign near 57 K. Our deconvolution of $\chi(T)$ cannot unambiguously separate temperature-independent terms, but we take this simultaneous change in sign as evidence that the deconvolution is meaningful. We prefer to think of the sign changes as associated with a gradual shift in the importance of the Landau diamagnetic and Pauli paramagnetic contributions to the susceptibility when a large-mass subset of the Fermi-surface electrons is removed by CDW energy gaps. Such a selective removal of large-mass electrons might be expected on portions of the Fermi surface having small curvature and effective nesting and would lead to a favoring of the diamagnetic susceptibility at lower temperatures.

In VSe_2 and other CDW materials, the magnetic

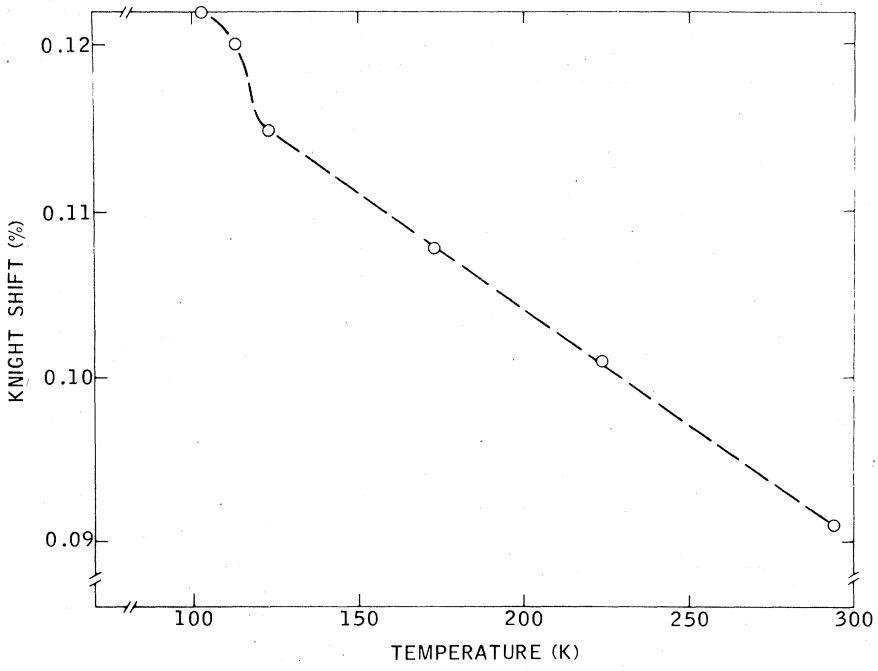

FIG. 6. Temperature dependence of the ^{77}Se Knight shift from 100 to 300 K.

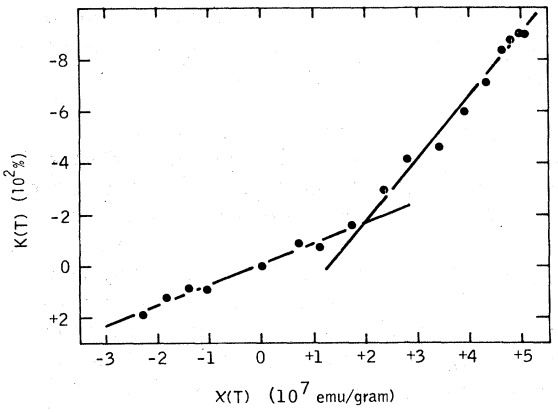

FIG. 7. Correlation between the ^{51}V Knight shift and the intrinsic magnetic susceptibility.

response of the material, reflected in R_H and χ, are among the most sensitive indicators of the CDW transitions. It is natural, therefore, to examine possible correlations between these parameters. As in the $(K(^{51}V), \chi_I)$ correlation, a (R_H, χ_I) analysis reveals *linear* relationships in *both* CDW states, as seen in Fig. 8. Only weak temperature dependences are seen above T_0 and a discontinuity and change in slope occurs at the transition from incommensurate to commensurate CDW states.

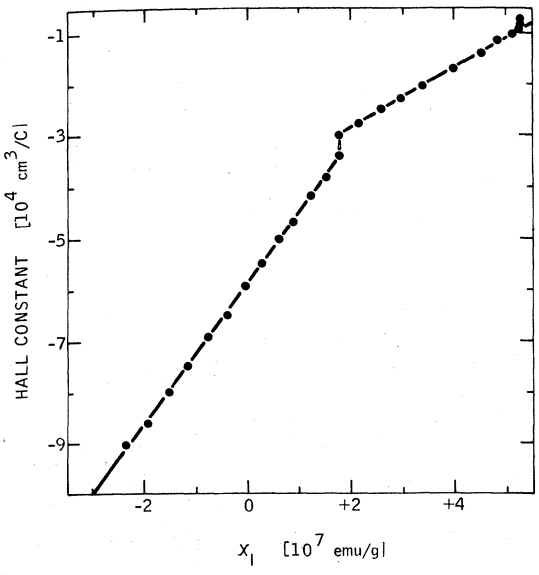

FIG. 8. Correlation between the Hall constant and the intrinsic magnetic susceptibility.

While some correlation between R_H and χ_I might be anticipated on the basis of previous observations in these CDW systems,[1] there is no present microscopic understanding of its source. However, several qualitative observations are in order. As for paramagnetic materials,[16] one can write $R_H = R_0 + 4\pi\chi_I R_m$, where R_0 is the normal Hall constant (directly related to the carrier concentration in the simplest case of a single-band model) and R_m is the additional contribution from the paramagnetic response of the system. Assuming such a single-carrier model, extrapolation of the data to $\chi_I = 0$ produces R_0 values expected for $\sim$1 electron/vanadium atom above T_d and $\sim$0.6 electron/vanadium atom below T_d. This change of $\sim$30% is consistent with previous estimates made by other means.[10] However, such a simple single-carrier picture for VSe_2 and even a simple multiple-carrier picture is probably unrealistic. Others[9] have observed that apparent changes in carrier concentrations at these transitions seem much too large when $R_H(T)$ and $\rho(T)$ are interpreted in terms of such simple models. Yet strikingly similar changes are often seen, e.g. in the R_H change for VSe_2 and $2H$-TaS_2.[1] Thus, the usual description of R_H in terms of one or more rigid bands of well-defined mobility appears inadequate for the present case.

An alternative explanation of the linear (R_H, χ_I) relationship could be based on microscopic inhomogeneities. Such crystalline inhomogeneities could produce microscopic CDW domains, either static or fluctuating. The density of states at the Fermi surface $[N(E_F)]$, the conductivity and the Hall constant would all scale with the density of such domains. In

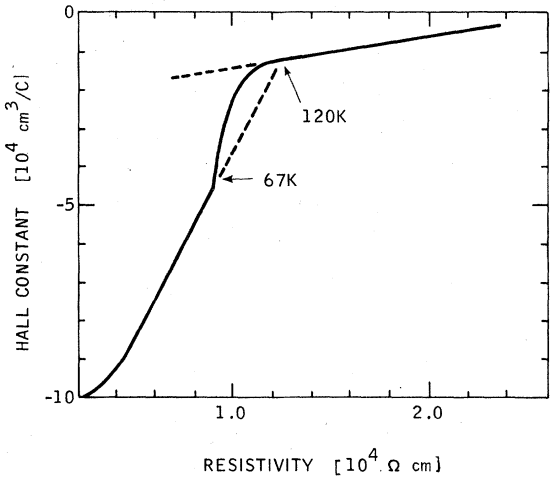

FIG. 9. Correlation between the Hall constant and the electrical resistivity of VSe_2.

the case where the various components (i.e., types of domain) have similar conductivities, $N(E_F)$, R_H, χ_I, and ρ should all scale approximately with the concentration of the components. While this might account for the linear (R_H, χ_I) relationship, it does not explain the (R_H, ρ) correlation seen in Fig. 9. While $R_H \propto \rho$ above T_0 and below T_d a striking departure from linearity is observed in the incommensurate CDW region.

IV. CONCLUSIONS

These observations lead to the following picture of VSe_2. Above the CDW transitions, VSe_2 behaves much like a usual d band metal: the magnitude of R_H suggests the presence of more than one type of carrier and χ_I, R_H, and $K(^{51}V)$ are nearly temperature independent. The $(K(^{51}V), \chi_I)$ correlation suggests changes in Fermi-surface density of states with temperature in the CDW states, and a change in Fermi-surface average hyperfine field at T_d. The (R_H, χ_I) correlation indicates the presence of an additional anomalous contribution to R_H, scaling with χ_I in both CDW regions with the effect most pronounced below T_d. Although the data presented here are in qualitative agreement with other reports, there are specific details and questions raised by these results including: (i) The peak in $\chi(T)$ often observed in VSe_2 is an artifact and the temperature of the peak is not related to the CDW onset temperature. (ii) The NMR results substantiate the existence of an onset transition near 110 K. (iii) The magnitude of R_H and ρ and proportionality between χ_I and R_H suggest that a non-conventional treatment of the transport properties will be required to explain temperature dependent scattering in the presence of CDW's. (iv) Correlations between the various transport and magnetic properties supply relatively unambiguous definitions of CDW transition temperatures.

ACKNOWLEDGMENTS

We gratefully acknowledge stimulating discussions of this work with H. M. McConnell, J. R. Schrieffer, and C. P. Slichter.

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