PHYSICAL REVIEW B VOLUME 23, NUMBER 2 15 JANUARY 1981

Magnetic studies of VSe_2

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(Received 2 May 1980)

The magnetic susceptibility of the layered compound VSe_2 is known to be very sensitive to preparation conditions. Preparation at temperatures above 580 °C produces interstitial (intercalated) V atoms that induce a paramagnetic moment and a Curie contribution to the susceptibility. We show that as the density of these defects increases, the charge-density-wave (CDW) onset temperature is decreased from 111 ± 1 K at a rate of 13 ± 3 K/at. % V interstitials, and the magnitude of the CDW anomaly in the susceptibility is also decreased. No evidence for further transitions below 111 K is obtained, although a small (0.2%) hysteresis is observed between 115 and 145 K. However, at present the source of this hysteresis is not understood.

INTRODUCTION

The occurrence of charge-density-wave (CDW) instabilities in the group V*b*, layered dichalcogenides, is well established.[1] In particular, 2*H*-$NbSe_2$ and 2*H*-$TaSe_2$,[2] as well as 1*T*-$TaSe_2$[3,4] and 1*T*-TaS_2,[4-6] have been studied extensively. However, few studies of 1*T*-VSe_2 have been published. This may be due to the fact that stoichiometric VSe_2 is difficult to prepare.[7] Thompson[8] pointed out that the properties of 1*T*-VSe_2 were somewhat unusual, even within the class of CDW materials, in that its properties were similar to the 2*H* polymorph of Nb or Ta chalcogenides, rather than to the structurally similar 1*T* polymorphs. Those studies that have been published are not in agreement with each other. This disagreement is apparent in measurements of the magnetic susceptibility[9-14] and especially in electron diffraction measurements of the temperature dependence and magnitude of the CDW wave vector.[14-19] These difficulties are very likely due to problems of nonstoichiometry. In this paper, we study the magnetic properties of both powder and single-crystal VSe_2 and detail the large effects that different preparation conditions have on the measured properties. In a companion study, the CDW lattice distortions are examined by x-ray diffraction.[17] These two studies provide the first detailed description of the intrinsic properties of VSe_2.

PREPARATION AND MEASUREMENT TECHNIQUES

VSe_2 may be more accurately described as $V_xV_{1-y}Se_2$, where x represents V atoms intercalated between VSe_2 layers and y represents V vacancies in the VSe_2 layer itself. Previous studies have shown that both x and y decrease with decreasing preparation temperature and increasing Se vapor pressure.[7] Consequently, low preparation temperatures should be used, consistent with reasonable reaction rates.

All the materials were prepared from V metal of 99.95% purity and Se shot of 99.999% purity in evacuated, sealed quartz tubes. Excess Se was added in every case to help ensure stoichiometry (≈ 1 mg/cm^2 of tube volume). Free-flowing single-phase powder samples were obtained after heating several days at 580 °C. Some samples were allowed to cool to near room temperature in 8 h by turning off the oven, while others were "quenched" into room-temperature air. Other samples were also prepared by heating to 800 °C for 1 week and were then air quenched. Single crystals were grown by iodine vapor transport in a gradient of 700 °C to 630 °C, the crystals growing in the cooler end of the tube.

The susceptibility was measured by the Faraday method using an He flow cryostat. Data were obtained in intervals of about 1 K while cooling at an average rate of 1 K/min. The absolute accuracy of the susceptibility is ± 2% as determined by a comparison to several standards. The relative accuracy of these measurements is much higher, ±0.06%, so that small changes versus temperature can easily be observed. The susceptibility of single crystals is measured using a knife edge and wedge arrangement that prevents the sample from rotating in the field. The sample used here was made by gluing a number of crystals together so that their basal planes were parallel. The hexagonal c axes were aligned to $\pm 1^\circ$ by this procedure, but no attempt was made to align the a axis.

RESULTS

The magnetic susceptibility (χ) of a powder sample of VSe_2 prepared at 580 °C and slowly cooled to room temperature is shown in Fig. 1 from 4.2 to 300 K. There is a sharp drop in χ near 115 K, and a Curie tail is apparent at low temperatures. Since this Curie tail is an import-

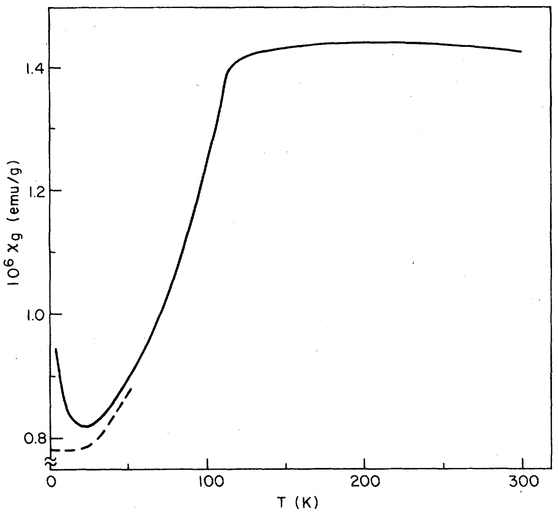

FIG. 1. Magnetic susceptibility of VSe_2 powder prepared at 580 °C and slow-cooled is shown from 4.2 to 300 K. The dashed curve is the measured susceptibility minus the Curie contribution.

ant indicator of the sample quality, we now consider this contribution to the susceptibility in some detail.

From previous work there is ample evidence that each V atom in the van der Waal's gap of VSe_2 produces a net paramagnetic moment of about 2.5 Bohr magnetons.[9,12,13] If we again use the formulation $V_xV_{1-y}Se_2$ for VSe_2, the value of x may be directly determined from the magnitude of the Curie tail. Below 20 K the data of Fig. 1 are well represented by $\chi_g = C_g/T + \chi_0$, where C_g is the Curie constant per gram and χ_0 is a constant. A least-squares fit of the data to this expression gives $C_g = 0.73\times10^{-6}$ emu K/g and $\chi_0 = 0.78\times10^{-6}$ emu/g. Using 2.5 Bohr magnetons per V and the value of C_g, we calculate $x = 0.000\,19$, a small value indeed. This value for interstitial V defects is lower than the impurity level expected from the purity of the starting V metal by a factor of about 3. However, the most likely impurity in V is Fe, and when Fe is substituted for V, it is nonmagnetic.[10] In our samples substitution will occur, rather than intercalation of the Fe, since the samples are prepared in excess Se. Thermodynamic data also indicate that $y \lesssim x$,[7] so that this material is very close to stoichiometry with very few vacancy or interstitial V defects. Having determined C_g, the Curie contribution may be subtracted from the data of Fig. 1 to obtain the intrinsic susceptibility of stoichiometric, defect-free VSe_2. The result is shown as a dashed line in Fig. 1 up to 50 K. In the discussion section, a more complete analysis of these data will be presented.

Of several samples prepared at 580 °C the Curie tail shown in Fig. 1 is the smallest measured. The largest was obtained from a sample prepared at 580°C and air quenched. The Curie constant for that sample was 2.0×10^{-6} emuK/g and $x = 0.000\,53$. For this same sample at low temperatures (< 20 K) $\chi_0 = 0.80\times10^{-6}$ emu/g, definitely larger than for the sample of Fig. 1. It appears, then, that even relatively low defect levels of 0.05% decrease the drop in susceptibility below 110 K.

When VSe_2 is prepared at 800 °C, even in excess Se, a compound of the approximate composition $V_{1.005}Se_2$ is obtained.[12,13] The susceptibility of material prepared at 800 °C is reexamined here in order to look for differences in the detailed behavior of samples prepared at 800 °C and 580 °C. The susceptibility of a powder sample prepared at 800 °C and air quenched is shown in Fig. 2. As expected the Curie contribution is very large, and the dip in susceptibility below 115 K is smaller. Again we subtract the Curie contribution in order to study the remaining susceptibility. However, when the Curie contribution is large, the method of determining this contribution is important, since the Curie contribution dominates the remaining contributions by several factors at low temperatures. Next we describe in detail the fitting procedure used in this case (and for all the other VSe_2 samples as well).

At low temperatures we fit the data to the expression

$$\chi_g = \frac{C_g}{T+\Theta} + \chi_0 , \tag{1}$$

where Θ is an effective interaction temperature reflecting either intersite exchange coupling or

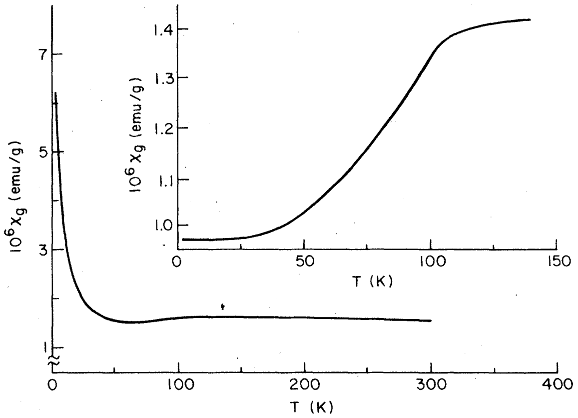

FIG. 2. Magnetic susceptibility of VSe_2 powder prepared to 800 °C and air-quenched is shown from 4.2 to 300 K. The inset shows the measured susceptibility minus the Curie contribution.

perhaps Kondo coupling of the moment with the conduction electrons. In order that the data at low temperatures do not dominate the fit, we minimize the fractional deviation of the data from Eq. (1). That is, we minimize

$$\epsilon^2 \equiv \sum \left(\frac{\chi\,(\text{calculated}) - \chi\,(\text{measured})}{\chi\,(\text{measured})} \right)^2$$

by a simple linear least-squares fit to obtain the best C_g and χ_0 for a range of assumed values of Θ. We use those values of Θ, C_g, and χ_0 which produce the smallest ϵ. We choose to fit the data of Fig. 2 to Eq. (1) over a temperature interval of 4.2 to 25 K, since the data of Fig. 1 suggest that considerable temperature dependence may develop in the supposedly constant term χ_0 above 25 K. However, the same values of χ_0, C_g, and Θ are obtained (±2%), whether we choose intervals of 10 to 20 K or 4.2 to 20 K. We find for the 30 actual data points below 25 K that $C_g = 26.8 \times 10^{-6}$ emu K/g, $\chi_0 = 0.97 \times 10^{-6}$ emu/g, $\Theta = 0.0 \pm 0.1$ K, and $\epsilon = 0.0026$. The interstitial V concentration x as calculated from the Curie constant is 0.0071. The inset in Fig. 2 shows the data corrected for the Curie contribution. Again, as in Fig. 1, the data are smooth and continuous, showing no jumps or breaks in slope at any temperature. However, there are some differences between the data shown in the inset of Fig. 2 and those of Fig. 1. First, the decrease in susceptibility below 115 K is clearly smaller in the 800 °C sample ($\chi_0 = 0.97 \times 10^{-6}$ vs 0.78×10^{-6} in Fig. 1). Second, the "rapid" decrease in susceptibility occurs about 10 K lower in the 800 °C sample.

Finally, we present the results of the measurement of the susceptibility of the single crystals. The susceptibility at room temperature was found to be isotropic (±2%), in contrast to $2H$-$TaSe_2$ (Ref. 20) and $2H$-$NbSe_2$,[21] where rather large anisotropies are observed. A small anisotropy of about 6% is reported in Ref. 14. The Curie tail was least-squares fitted and we found $C_g = 6.7 \times 10^{-6}$ emu K/g and consequently $x = 0.0018$. The interstitial V content is higher than in the powder samples prepared at 580 °C, consistent with the higher growth temperature of 630 °C. At lower temperatures the rate of crystal growth decreased rapidly, and temperatures of 630 °C or higher were necessary to obtain crystals of reasonable dimensions (≈5 mm) and mass. Single crystals from this same growth were used in the x-ray diffraction study of VSe_2.[17]

DISCUSSION

In this section we examine in some detail the data presented in the previous section. First consider the data of the most stoichiometric VSe_2. There is a small sample-dependent hysteresis in the susceptibility of VSe_2 between 115 and 145 K as shown in Fig. 3 for the same sample as that used to obtain Fig. 1. In two other samples prepared at the same temperature and air quenched, no hysteresis was observed to within our resolution (±0.06%). However, we report this hysteresis both because this sample showed the smallest Curie contribution (thus the hysteresis may be intrinsic to the best materials) and because a distinct decrease in susceptibility is observed near 145 K when some of the V is substituted by Nb.[22] The data suggest that some weak first-order transition occurs near 145 K. However, diffraction evidence shows that the CDW onset temperature is near 110 K, where the susceptibility drops sharply.[17] At present we have no suggestion concerning the nature of the 145 K transition.

In an attempt to discover other anomalies in the data, we calculated the numerical derivative by fitting the data several points at a time to a quadratic polynomial. The first derivative (Fig. 4) shows a peak at 111 ± 1 K. Since this is close to the point at which the superlattice intensity observed in the x-ray diffraction study decreases to zero, we take this to be the CDW onset temperature. As is apparent from both Fig. 1 and Fig. 4, the data are smooth below 110 K, showing no discontinuous breaks. This is in marked contrast to some previously published data. These authors reported a discontinuous decrease in the susceptibility and a change in slope near 70 K, and suggested that this may be due to a transition to a commensurate CDW state.[9,12,22] No such transition is observed in x-ray diffraction[17] nor is it reflected in these data.

The effects of nonstoichiometry are apparent

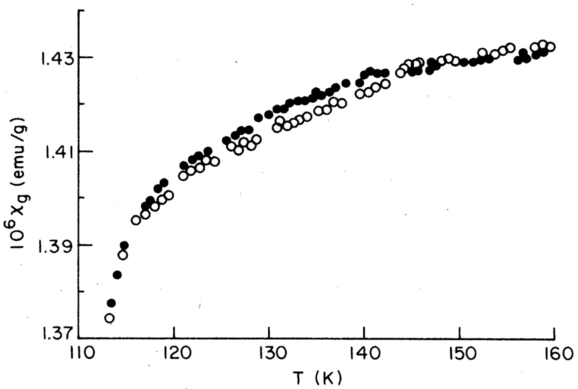

FIG. 3. Magnetic susceptibility of Fig. 1 on an expanded scale shows a small hysteresis between 115 and 145 K. The solid points are obtained while cooling and the open points while warming.

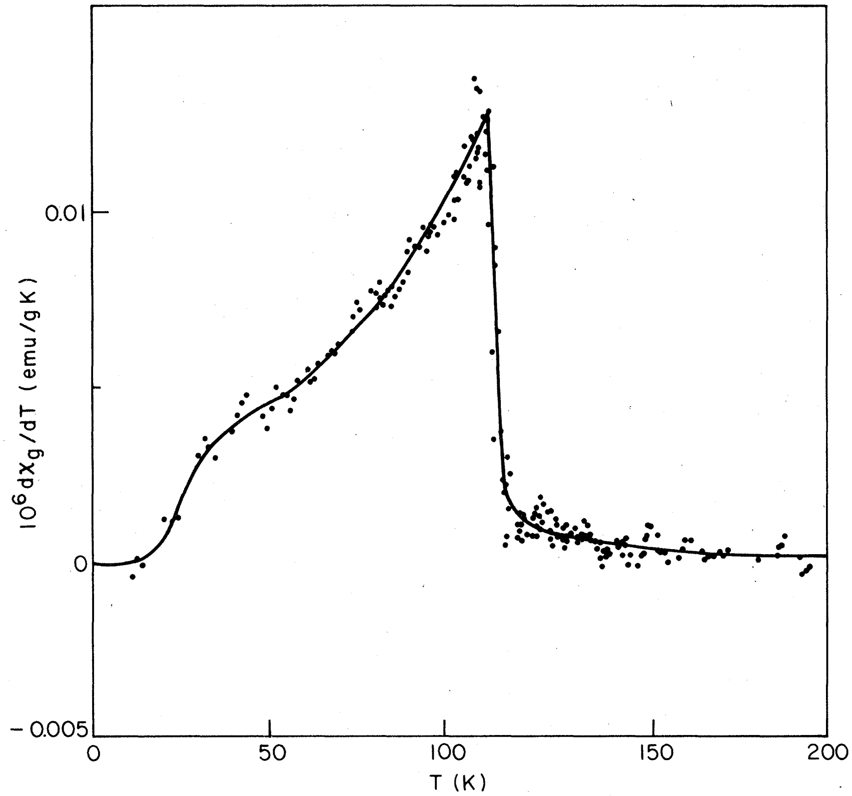

FIG. 4. Numerical derivative of the data of Fig. 1 shows a peak at 111 ± 1 K, which we take to be the CDW onset temperature.

from the inset of Fig. 2. A much reduced and broader peak is observed in the derivative of the corrected data at 102 ± 2 K and no other anomalies are seen. If we assume that the CDW onset temperature T_0 is linearly suppressed by nonstoichiometry, we estimate from the derivative data that $dT_0/dx = 13 \pm 3$ K/at.%. The expected CDW transition temperature of the single crystals grown at 630 °C can be estimated from the degree of nonstoichiometry obtained from the magnitude of the Curie contribution. We estimate that the onset temperature for the crystals should be 108.7 ± 0.5 K, in close agreement with the value of 108.6 K determined by x-ray diffraction. This gives us confidence that the peak in the derivative of the susceptibility is indeed the proper quantity to use in the determination of the onset temperature.

As previously pointed out, the size of the CDW-induced susceptibility anomaly [i.e., $\chi(T_0) - \chi(4.2\text{ K})$ after correction for a Curie contribution] also decreases with increasing nonstoichiometry. Although interstitial defects and vacancies may suppress this anomaly at different rates, we can estimate the effect of nonstoichiometry from the data of Figs. 1 and 2. These data suggest a decrease in the size of the anomaly of about 0.27×10^{-6} emu/g at.% of interstitial vanadium. This estimate is in reasonable agreement with that determined from the disappearance of the CDW in highly nonstoichiometric $V_{1+x}Se_2$ samples at $x = 0.03$ (Ref. 13) and with the small decrease in the anomaly reported in this paper at $x = 0.0005$.

We suggest that the different CDW wave vectors observed in electron diffraction on different samples are due to the different preparation temperatures of the samples studied. Those samples prepared at higher temperatures[14-16] have a higher defect density and show diffraction patterns distinctly different from those prepared at low temperatures.[17-19] We note that electron diffraction studies of crystals from the same batch as those used for our x-ray diffraction studies[17] show the same CDW wave vector[18] as the x-ray studies.

CONCLUSIONS

The physical properties of VSe_2 are very sensitive to preparation conditions; higher preparation temperatures produce both interstitial (intercalated) V and V vacancies in the nominally full V layer.[7] The interstitial V atoms induce a paramagnetic moment in VSe_2 and their concentration can be easily measured by magnetic susceptibility.[9–14] We find for the most stoichiometric samples (interstitial concentration of $V \lesssim 0.02\%$) that the CDW onset temperature corresponds to a peak in the derivative of the susceptibility at 111 ± 1K. No other anomalies are observed in the susceptibility or its derivative *below* this onset temperature. This observation is in agreement with recent single-crystal x-ray diffraction studies in which only one transition is observed at the CDW onset temperature.[17] However, a small hysteresis ($\approx 0.2\%$) is observed in the susceptibility between 115 and 145 K, suggesting some very weak first-order transition at 145 K. At present we do not understand the nature of this transition. The anomaly at 145 K appears to be enhanced by the substitution of V with other transition elements such as Nb.[22] When VSe_2 is prepared at temperatures above approximately 580 °C, significant deviations from stoichiometry occur, which reduce both the CDW onset temperature and the decrease in the susceptibility below the onset temperature (after correction for the Curie contribution). At high enough preparation temperatures (>800 °C) a large concentration of atomic defects is produced, and we suggest that the difference in defect concentrations is responsible for the difference in reported electron diffraction patterns.[14–19]

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