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THE EFFECT OF Fe SUBSTITUTION ON THE CHARGE DENSITY WAVE IN VSe₂

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Abstract. — We compare the effect of Fe substitution in V₁₋ₓFeₓSe₂ with the previously measured properties of 1T-Ta₁₋ₓFeₓSi₂. In pure VSe₂ a Charge Density Wave (CDW) appears below $T₀ = 112 \text{K}$, while the CDW in 1T-TaSe₂ occurs below $T₀ ≈ 600 \text{K}$. Several phenomena associated with Fe substitution are observed in 1T-Ta₁₋ₓFeₓSe₂:

1. the CDW is stable at 300 K for $x ≤ 0.15$;
2. the commensurate CDW state is suppressed at $x ≈ 0.06$;
3. the CDW is eliminated when approximately 3% Fe is substituted for V.

1. Introduction. — We present recent studies of the effects of cation substitution on the Charge Density Wave (CDW) transition in VSe₂. These results are compared to those obtained in TaSe₂ [1, 2, 3] and to the ideas expressed in phenomenological Landau theories [2, 4]. In order to make an orderly comparison, some of our previous results will be first reviewed.

A Charge Density Wave is a periodic static distortion of the lattice and conduction electron density that occurs in most of the metallic layered compounds below an onset temperature $T₀$. The wave vector of this distortion, $q$, is determined by the Fermi surface and is generally incommensurate with the lattice. Frequently, the $q$ changes slightly to become commensurate with the lattice in a first order transition at $Tₐ < T₀$.

Table I lists some of the CDW unstable layered compounds with the onset temperature $T₀$, lock-in temperature $Tₐ$, and approximate CDW wavelength ($λ = 2π/q$). VSe₂ has the largest $λ$ and the lowest $T₀$ of the 1T structure compounds. Here we will compare the properties of VSe₂ to those of 1T-TaSe₂ since the structures are the same, and to 2H-TaSe₂ since the physical properties are quite similar to those of VSe₂ [5]. We find that the CDW state of VSe₂ is very sensitive to cation disorder, the CDW state is eliminated when approximately 3% Fe is substituted for V.
2. Effects of doping in 1T-TaSe₂ — The magnetic susceptibility (\(\chi\)) of 1T-TaSe₂ and 2H-TaSe₂ is given in figure 1 and the electrical resistivity (\(\rho\)) in figure 2. The wide difference in the properties of these polymorphs is due in part to their different band structure [8] and to the possible different mechanisms for CDW formation [9]. Here we note the primary differences:

1) \(\chi\) of 2H-TaSe₂ shows strong Pauli paramagnetism both above and below \(T_\theta = 122\ K\), while 1T-TaSe₂ is diamagnetic below \(T_\theta \approx 600\ K\).

2) The resistivity of 2H-TaSe₂ drops rapidly below \(T_\theta = 122\ K\), while the resistivity of 1T-TaSe₂ is larger than that of 2H-TaSe₂ even at high temperatures (\(\sim 500\ K\)).

The difference below \(T_\theta\) are also related to the fraction of Fermi surface destroyed by the CDW induced gaps. In 1T-TaSe₂ approximately 90% of the Fermi surface is lost, while in 2H-TaSe₂ 15% or less is lost [3, 10].

The effects of cation substitution have been studied in 1T-TaSe₂ since in most cases even very small substitution appears to make the 2H polymorph unstable [3]. Cation substitution has been used to show that decreasing conduction electron concentration decreases the CDW wavelength, for example in 1T-Ta₁₋ₓTiₓSe₂ [1, 3]. Cation substitution also produces disorder. The effects of disorder in 1T-TaSe₂ are threefold:

1) The onset temperature is slowly reduced.

2) The lock in temperature is rapidly reduced. The commensurate state does not occur beyond a critical doping level, as illustrated in figure 3. The effects of doping on \(T_\theta\) and \(T_d\) agree at least qualitatively with the Landau model proposed by McMillan [4].

3) The low temperature resistivity is greatly increased over that of the pure material (see Fig. 3). For some dopants, the resistivity is infinite at zero temperature when the doping is beyond a certain minimum level [11]. For example in 1T-Ta₁₋ₓFeₓSe₂ the resistivity for \(x \gtrsim 0.15\) diverges at low temperatures as shown in figure 4.

This last case of Fe doping is particularly interesting. Mössbauer data show that the Fe is divalent in 1T-Ta₁₋ₓFeₓSe₂ [12]. 2 \(x\) of the Ta atoms become pentavalent for overall charge compensation, reducing the conduction electron density to 1-3\(x\) of that in 1T-TaSe₂. Consequently, semiconducting like properties at \(x = \frac{1}{2}\) are not unexpected. However when \(0.15 < x < \frac{1}{2}\), the loss of electron mobility at low temperatures is due to the interaction of increasing randomness and decreasing occupied bandwidth. Within simple models, the localization occurs when the amplitude of the random part of the potential
Fe SUBSTITUTION IN VSe₂

FIG. 4. - The random potential of some dopants, such as Fe in 1T-Ta₁₋ₓFeₓSe₂, produce Anderson localization of the remaining carriers at low T when \( x > x_c \).

is equal to the bandwidth. Landau theories predict that the impurity potential close to a CDW instability will be strong and long range \([4]\), rather than being screened out in a short Thomas Fermi length, as in normal metals. The CDW enhances the random potential over what is obtained in normal metals, producing Anderson localization \([3]\) when the concentration of Fe, Co, or Ni is above a critical amount in 1T-TaSe₂ \([11]\).

Finally we note that 1T-Ta₁₋ₓFeₓSe₂ (or Seₓ) exhibits a low spin to high spin transition of the Fe²⁺ with increasing temperature \([12]\), as observed for example in the magnetic susceptibility of 1T-Ta₀.₃Fe₀.₁Se₂ (Fig. 5). This transition occurs when the crystal field \((10 \, Dq)\) and Hund’s rule energy \( (E_H) \) are close to equal. The crystal field is determined primarily by the near neighbour Se positions and distances from the Fe, and the latter parameters are fixed by the parent 1T-TaSe₂ lattice. From the measurements we know that \( A = 10 \, Dq - E_H \) is small at high temperatures \((T \gtrsim T_0)\). However, \(10 \, Dq\) is expected to have an unusual temperature dependence due to the large amplitude of the CDW \((\approx \text{one electron/atom})\) attained well below \( T_0 \) \([14, 15]\). We find that \( A\) in fact increases at low temperatures, rapidly cutting off the high spin state.

In the case of the 1T polytypes it is evident that not only does cation doping effect the CDW but also the CDW effects the magnetic behaviour and the scattering potential of the dopants. Since the variety of phenomena observed is so large in the case of Fe doping in 1T-TaSe₂, we have begun a comparative study of 1T-V₁₋ₓFeₓSe₂.

3. Sample preparation. — Powder samples were prepared from the elements by reaction at 650 °C in a small excess of Se. The samples were homogenized by grinding the reacted powder and pressing into pellets with subsequent reheating at 650 °C (twice). At higher reaction temperatures V₁₋ₓSeₓ forms with \( x > 0 \) even when prepared in excess Se. Single crystals were grown by iodine vapor transport from these powders, again in excess Se, at a growth temperature of 650 °C.

The 1T structure is retained for Fe substitution up to \( x = \frac{1}{3}(V_{1/3}Fe_{2/3}Se_2)\). No extra lines are observed in powder X-ray diffraction, indicating that the Fe substitution is random, as in 1T-Ta₁₋ₓFeₓSe₂ \([3]\). Magnetic susceptibility indicates that Fe is divalent and low spin (see later). At \( x = \frac{1}{3} \) we would expect all the V to be pentavalent, and further substitution impossible. However, in VSe₂ the V d-band and Se valence band overlap, as shown by photoemission \([16]\). So that as the d-band is emptied by production of V⁵⁺ holes are produced in the valence band. At \( x = \frac{1}{2} \) there should be 0.5 holes per Se atom.

4. Results. — The magnetic susceptibility and resistivity of pure VSe₂ are shown in figure 6. An anomaly

![Fig. 4](image1.png)

![Fig. 5](image2.png)

![Fig. 6](image3.png)
is apparent in both properties at the CDW onset temperature, $T_0 = 112$ K. While VSe$_2$ has a 1T structure, the CDW anomalies have some similarity to those of 2H-TaSe$_2$ (see Figs. 1 and 2) [17]. At $T_0$ the anomalies in these properties are too weak to be seen on this scale [5]. From the decrease in $\chi$ below $T_0$ and the increase in $\rho$, we estimate that approximately 30% of the Fermi surface is lost in the CDW transition. This latter fact, along with the lower $T_0$, suggests that the CDW has a smaller amplitude in VSe$_2$ than in 1T-TaSe$_2$.

When Fe is substituted for V the CDW onset temperature and amplitude are rapidly suppressed, as determined by the magnetic susceptibility (Fig. 7).

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**Fig. 7.** The magnetic susceptibility of $V_{1-x}Fe_xSe_2$ powders clearly shows the suppression of $T_0$ and $\Delta \chi$, the decrease in $\chi$ below $T_0$. $T_0 = 0$ at $x \approx 0.035$. Small Curie contributions, comparable to that shown in Fig. 6, were subtracted from the data.

We estimate that $T_0 = 0$ at $x = 0.035$. The smooth but small decrease in $\chi$ observed when $x > 0.035$ is probably related to the decrease in the density of states at the Fermi level induced by local distortions about the V sites. These distortions will occur even above $T_0$, or, as in the case here, when the CDW is incipient (not quite stable) [4].

The suppression of $T_0$ is almost as rapid when Ti is substituted for V as shown in Fig. 8. Ti valence is $4^+$ and does not produce $V^{5+}$ for charge compensation as does Fe. But even for this weak perturbation of the order in VSe$_2$, $T_0$ is reduced to zero at $x$ approximately 0.05.

At large $x$, the low temperature susceptibility increases rapidly and is given by $\chi(T) = \chi_0 + C/T$, where $\chi_0$ is a constant (see Fig. 9). The Curie constant, $C$, gives a $\mu_{eff}$ of 0.6 $\mu_B$ and 0.7 $\mu_B$ per Fe at $x = \frac{1}{2}$ and $\frac{1}{4}$ respectively. This moment could arise in several ways:

1) each Fe has the low moment calculated;
2) a small amount of Fe or V is in the Van der Waals region between the layers. In this case either would be magnetic ($Fe^{2+}S = 2$, or $V^{3+}S = 1$) [18].

The latter possibility [2] seems most likely, since even stoichiometric VSe$_2$, itself is difficult to prepare. The paramagnetic $\chi_0$ obtained for these two samples may arise from two sources: the Pauli paramagnetism of the expected Se holes and the van Vleck paramagnetism of the Fe$^{3+}$ ion.

There is no evidence at any Fe concentration of a low spin to high spin transition of the Fe with increasing temperature. This is not surprising for two reasons:

1) The Fe-Se bond length imposed by the parent VSe$_2$ lattice is shorter than in 1T-TaSe$_2$. Thus 10 $Dq$ will be larger.
2) The modulation of 10 $Dq$ by the CDW will be weaker in VSe$_2$ than in 1T-TaSe$_2$.

The electrical resistivity of 1T-$V_{1-x}Fe_xSe_2$ crystals is shown figure 10 for current parallel to the layers. The anomaly signifying the CDW onset is rapidly lost as expected. By $x < 0.1$ the impurity scattering is quite large, even though the CDW is fully suppressed...
Fe SUBSTITUTION IN VSe$_2$

CONCLUSIONS.

V$_{1-x}$Fe$_x$Se$_2$ has the CdI$_2$ (1T) structure for $x \leq \frac{1}{2}$. Since the Fe appears to be divalent (low spin), at large $x$ the formal selenium valence must be less than 2$^{-}$ and the V will be 5$^{+}$. This is not unexpected, since the V d-band and Se p-band overlap, and at $x = \frac{1}{2}$ we expect 0.5 holes per Se.

The CDW state in VSe$_2$ is eliminated by a small amount of cation substitution ($\approx 3\%$). In contrast to 1T-Ta$_{1-x}$Fe$_x$Se$_2$, no low spin-high spin transition is observed in 1T-V$_{1-x}$Fe$_x$Se$_2$. We have not observed an increasing resistivity at low temperatures expected from a possible Anderson localization, but the measurements are yet to be extended to higher Fe concentrations than $x = 0.2$.

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References

[17] We note that isostructural LiTlSe$_2$ has a large Pauli paramagnetic susceptibility and a decrease at low temperatures similar to VSe$_2$, see Murphy, D. W., Di Salvo, F. J., Hull, G. W., Jr. and Waszczak, J. V., Inorg. Chem. 15 (1976) 17.
[18] In all layered compounds studied to date Fe has a magnetic moment when intercalated, see for example: Eibschütz, M., Di Salvo, F. J., Hull, G. W., Jr. and Mahajan, S., Appl. Phys. Lett. 27 (1975) 464. The intercalated V in V$_{1-x}$Se$_2$ is also known to have a magnetic moment, see for example: Silbernagle, B. G., Thompson, A. H. and Gamble, F. R., 20th Annual Conf. on Magnetism and Magnetic Materials, AIP Conf. Proceedings 24 (1975) 380.
[19] In Landau models the free energy difference between a CDW state with amplitude $\psi$ and the normal state is approximately (to lowest order) $\Delta F = F_{\text{CDW}} - F_{\text{normal}} \propto (T - T_0)^{1/4}$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$. McMillan showed (Ref. [4]) that an impurity will induce a large local $\psi_{\text{imp}}$ even above $T_0$ where $\Delta F > 0$, with $\psi_{\text{imp}} \propto (T - T_0) \psi^2$.