

## Local moments in the paramagnetic phase of dilute CrV alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 1761

(<http://iopscience.iop.org/0953-8984/6/9/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 17:47

Please note that [terms and conditions apply](#).

## Local moments in the paramagnetic phase of dilute CrV alloys

P Hill†, Naushad Ali†, A J A de Oliveira‡, W A Ortiz‡, P C de Camargo§ and Eric Fawcett||

† Physics Department, Southern Illinois University, Carbondale, IL 62901-4401, USA

‡ Departamento de Física, Universidade Federal de São Carlos, São Carlos, SP 13565-905, Brazil

§ Departamento de Física, Universidade Federal do Paraná, Curitiba, PR 81531-970, Brazil

|| Physics Department, University of Toronto, Toronto M5S 1A7, Canada

Received 12 August 1993

**Abstract.** The magnetic susceptibility of Cr+0.2 at.% V and Cr+0.4 at.% V alloys (nominal concentrations) is found to show a sharp increase at the Néel temperature with increasing temperature and to obey a Curie–Weiss law in the paramagnetic phase up to 400 K, corresponding to a moment per V atom of about one Bohr magneton. The relation of these results to the behaviour of other physical properties of dilute CrV alloys is discussed.

### 1. Introduction

It is well known that a local moment exists at the impurity atom in the paramagnetic phase of dilute alloys of Cr with the ferromagnetic metals Fe and Co [1, 2], as confirmed subsequently by several researchers [3], and with the antiferromagnetic metal Mn [4]. The only other impurity that shows clear evidence of having a local moment above the Néel temperature  $T_N$  is V [5]. Antiferromagnetic alloys of Cr with Re [6, 7], Rh [8] and Si [9] also show some evidence of local moments above  $T_N$  in that, for concentrations high enough to be well into the commensurate spin-density-wave (SDW) phase, there are some alloy compositions for which the susceptibility decreases with increasing temperature in the paramagnetic phase. For no impurity except Fe [2] does the susceptibility show a Curie–Weiss temperature dependence in the antiferromagnetic phase [3], thus demonstrating coexistence of the local moments with the SDW [10] in this unique case.

This behaviour of the V impurity atom is most surprising, since V metal shows no magnetic order. In fact, V dissolved in Cr is generally regarded as simply an agent for changing the electron concentration by virtue of the different number of electrons per atom, thereby tuning the Fermi level across the SDW energy gap [11], and at the same time reducing the magnitude of the gap by increasing the mismatch between the nesting electron and hole Fermi surfaces [12].

### 2. Experimental details

Our two CrV samples were prepared by a float-zone method that combines both radio-frequency and resistance heating [13]. A single crystal of the Cr+0.2 at.% V sample had been thoroughly characterized in previous experiments [14–16]. Polycrystal samples were also available, which were taken from material near the melted zone, and thus had been

annealed close to the melting point for an hour. The Cr+0.4 at.% V samples also appear to be high-quality crystals of uniform composition, as evidenced by the similarly sharp Néel transition.

The magnetic susceptibility data presented here were measured on polycrystal samples in a SQUID magnetometer supplied by Quantum Design, over the temperature range 5–40 K and in an external field of 1 kG. Measurements were also made on both single-crystal and polycrystal samples, with no apparent difference, by use of an AC susceptometer [17]. This was a modified Hartshorn bridge [18], which provides both the real and imaginary parts of the susceptibility. A study of hysteresis was made in both samples and in pure Cr with this set-up, by sweeping the temperature at a rate of about  $0.3 \text{ K min}^{-1}$  in both directions from 220 K to 350 K, but none was found to within  $\pm 0.1 \text{ K}$ .

### 3. Results and discussion

The temperature dependence of the magnetic susceptibility  $\chi$  shown in figure 1 is quite different for the alloys from that for pure Cr. We shall consider first the behaviour in the paramagnetic phase above the Néel temperature  $T_N$ , where  $\chi$  increases with temperature for Cr, whereas for the alloys it decreases in a manner suggestive of a Curie-Weiss law, corresponding to there being a moment on the V atom.

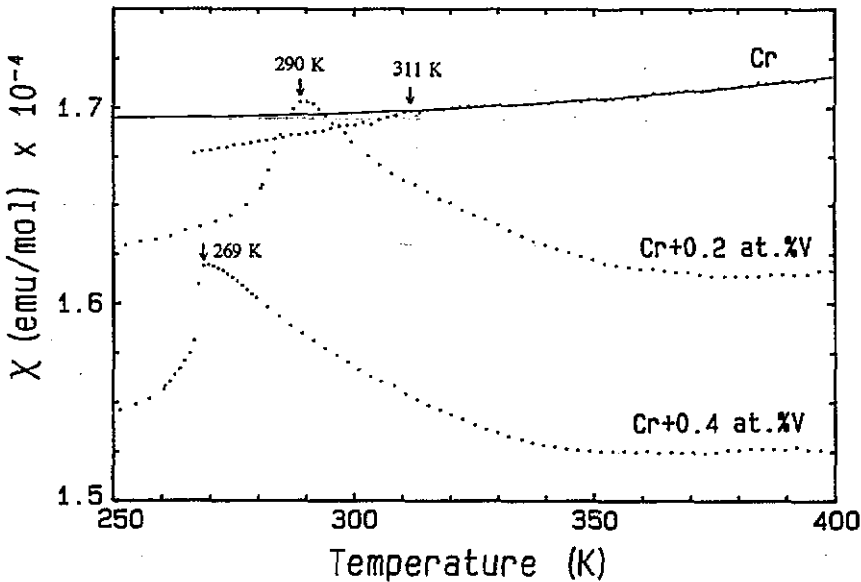


Figure 1. Temperature dependence of the magnetic susceptibility  $\chi$  for pure Cr (the line through the data points above the Néel temperature,  $T_N = 311 \text{ K}$ , is a quadratic fit, as described in the text, and is extrapolated below  $T_N$  to provide a reference for the alloy samples), and for the two Cr alloy samples as labelled. The position and value of  $T_N$  for each sample is indicated.

The experimental results were analysed accordingly, first by fitting the pure Cr data with a function quadratic in temperature

$$\chi(\text{Cr}) = \chi_0 + a_1 T + a_2 T^2 \quad (1)$$

then, by assuming additivity of the two contributions to the susceptibility  $\chi(A)$  of the alloy A of composition Cr+x at.% V, and writing

$$\chi(A) = x\chi(V) + (1-x)[\chi(\text{Cr}) - \Delta\chi(A)] \quad (2)$$

and, finally, by using the Curie-Weiss law to describe the temperature dependence of the contribution  $\chi(V)$  of the moment  $p$  on the V atom

$$\chi(V) = N_A p \mu_B^2 / 3k_B (T - \theta_N). \quad (3)$$

In (2) we include a term  $\Delta\chi(A)$  corresponding to the fact that alloying Cr with V produces an overall temperature-independent decrease of  $\chi$  in the paramagnetic phase, as well as the Curie-Weiss-law term. The concentration  $x$  at.% V for alloy A was determined from  $T_N(A)$ , which in  $\text{Cr}_{1-x}\text{V}_x$  alloys decreases linearly with  $x$  until  $T_N = 0$  for  $x = 3.8$  at.% V [3]. The Néel temperatures,  $T_N = 290$  and  $269$  K, for the alloys of nominal composition, Cr+0.2 at.% V and Cr+0.4 at.% V, respectively, give the actual concentrations of V,  $x = 0.26$  and  $0.51$  at.% V, respectively.

The Curie-Weiss temperature  $\theta_N$  in (3), together with the moment  $p$  on the V atom and  $\Delta\chi(A)$ , provides three variable parameters to make a least-squares fit to the data. Three different methods, which correspond to different interpretations of the quantities in (2), were used to subtract the susceptibility of the alloy from that of pure Cr in order to obtain the contribution of the V moment:

(I) the 'shift' method makes  $T_N(A)$  coincide with  $T_N(\text{Cr})$  by shifting the alloy data along the temperature axis in figure 1, so that the data point for  $\chi_A$ , at a given  $T > T_N(A)$ , is substituted in (2) along with the value on the quadratic curve of (1) fitted to the Cr data at temperature  $T + \Delta T(A)$ , with  $\Delta T(A) = T_N(\text{Cr}) - T_N(A)$ ;

(II) the 'direct-comparison' method compares  $\chi(A)$  with the value of  $\chi(\text{Cr})$  at the same temperature,  $T > T_N(A)$ , by using the extrapolation below  $T_N(\text{Cr})$  of the curve fitted to the Cr data and described by (1);

(III) the 'reduced-temperature' method compares  $\chi(A)$  at temperature  $T > T_N(A)$  with the value from the curve fitted to the Cr data at the same reduced temperature,  $T(\text{Cr})/T_N(\text{Cr}) = T/T_N(A)$ .

The values in  $\text{emu mol}^{-1}$  of the terms in (1) that give the curve fitted to the Cr data shown in figure 1 are  $\chi_0 = 1.75 \times 10^{-4}$ ,  $a_1 = 4.54 \times 10^{-8} \text{ K}^{-1}$  and  $a_2 = 9.17 \times 10^{-11} \text{ K}^{-2}$ . The values of  $p$ ,  $\theta_N$  and  $\Delta\chi$  obtained by each of three methods for the two alloys are given in table 1. The shift method (I) gives values of  $p$  and  $\theta_N$  close to the average values for the three methods. This would in fact seem to be the most physically reasonable of the three. The direct-comparison method (II) involves a somewhat arbitrary extrapolation of the fit to the Cr data in the paramagnetic phase to temperatures well below  $T_N$ , while the reduced-temperature method (III) makes the unwarranted assumption that the temperature dependence of  $\chi$  in the paramagnetic phase is a function of the reduced temperature relative to the Néel temperature of the alloy.

Figure 2 shows the fit of the data to a Curie-Weiss law for the contribution  $\chi(V)$  obtained by the shift method. For each alloy the correlation coefficient of the fit is 0.996. The moment on the V atom decreases from about  $1.5 \mu_B$  for Cr+0.2 at.% V ( $x = 0.26$  at.% V) to  $1.0 \mu_B$  for Cr+0.4 at.% V ( $x = 0.51$  at.% V). This is consistent with the trend found by Kondorskii *et al* [5], who obtained values  $p = 1.8, 1.4$  and  $1.1 \mu_B$  for  $x = 0.6, 1.0$  and  $1.5$  at.% V, respectively. The method of analysis employed by Kondorskii *et al* was relatively crude,

Table 1. Magnetic moment  $p$  on the V atom, Curie-Weiss temperature  $\theta_N$  and overall decrease  $\Delta\chi$  of the susceptibility in CrV alloys in the paramagnetic phase.

	Cr+0.2 at.% V			Cr+0.4 at.% V		
$x$ at.% V	0.26			0.51		
$T_N$ (K)	290			269		
Method	$p$ ( $\mu_B$ )	$\theta_N$ (K)	$\Delta\chi$ ( $10^{-5}$ emu mol $^{-1}$ )	$p$ ( $\mu_B$ )	$\theta_N$ (K)	$\Delta\chi$ ( $10^{-5}$ emu mol $^{-1}$ )
I	1.46	251	2.09	1.00	236	2.34
II	1.34	254	1.33	0.83	245	2.11
III	1.56	247	1.50	1.21	224	2.56
Average	1.45(11)	250	1.64	1.02(19)	235	2.34

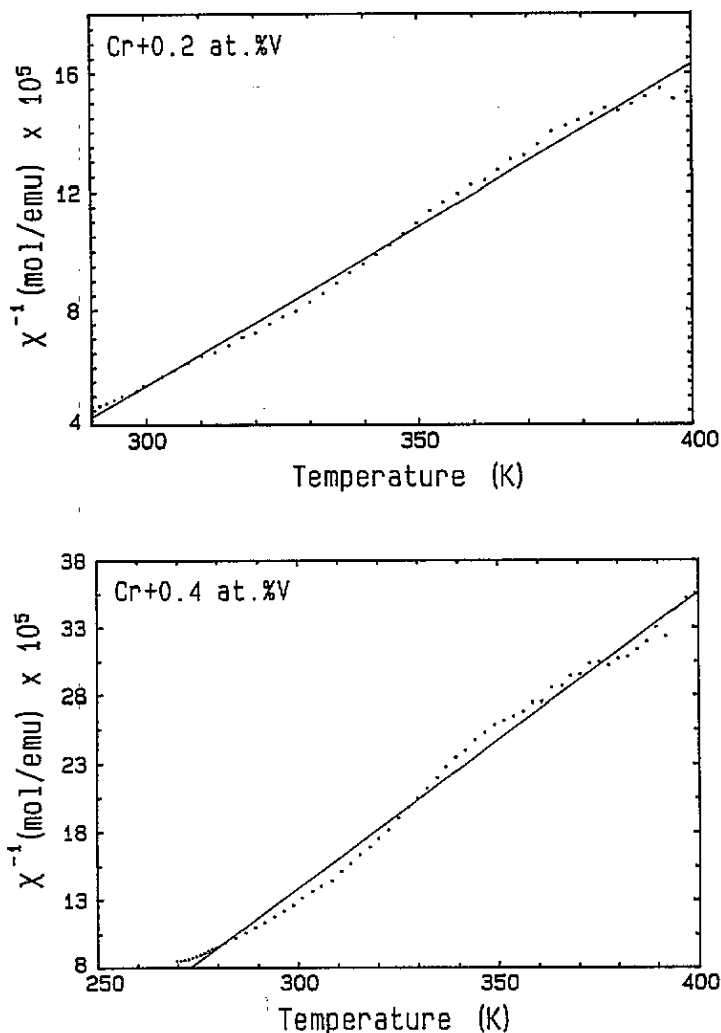


Figure 2. Temperature dependence of the reciprocal of the contribution  $\chi(V)$  of the V atoms to the susceptibility obtained by use of (3), which gives the values of  $p$ ,  $\theta_N$  and  $\Delta\chi$  listed in table 1 for the shift method (I).

which may account for the fact that their value of  $p$  for  $x = 0.6$  at.% V is almost twice ours for  $x = 0.5$  at.% V.

The existence of the term  $\Delta\chi(A)$  in (2), and the fact that, as seen in table 1, it increases roughly proportionately with the V concentration, may be explained as follows. As the electron concentration decreases on doping group VI Cr with the group V metal V, and with it the Fermi level, the density of states at the Fermi surface will, according to band-structure calculations [19], initially decrease. Thus the temperature-independent Pauli susceptibility might be expected to decrease.

We turn now to the other very surprising feature of our experimental data, namely the sharp increase in magnetic susceptibility with increasing temperature at the Néel transition, which is seen in each of the CrV alloys illustrated in figure 1. This behaviour is in strong contrast with that seen in pure Cr, also shown in figure 1, which is typical of all other dilute alloy samples previously measured, including CrV alloys [5, 20].

There is renewed interest in the nature of the Néel transition in Cr and its dilute alloys. In pure Cr the transition is weakly first order, with an abrupt onset of the SDW at the Néel temperature, as seen in neutron diffraction [16, 21]. Similar behaviour, as reviewed in [3], is seen in the thermodynamic properties, specific heat [22] and thermal expansion [23], with the picture for the elastic moduli being obscured by the strong attenuation close to  $T_N$  for those that show large effects associated with the SDW [24].

Critical fluctuations are seen in pure Cr around the Néel transition in all these properties, but in the ordered phase below  $T_N$  the rapid increase in the magnitude of the order parameter with decreasing temperature soon dominates their temperature dependence. There is little evidence for critical fluctuations in the transport properties, but below  $T_N$  the rapid variation of the resistivity [25, 26] and the thermoelectric power [27] in the ordered phase is associated with the growth of the SDW with decreasing temperature. The anisotropy of the resistivity in the ordered phase [25, 26] shows that its rapid increase below  $T_N$  is due to the opening of a gap at the Fermi surface due to the formation of electron-hole pairs, in accordance with Overhauser's analysis [28] of the origin of the SDW in Cr.

The change in both resistivity and thermopower below  $T_N$  is so rapid that it is difficult to say whether or not there is a first-order jump. There appears in figure 1 to be no sign of a jump at  $T_N$ , nor any evidence of critical fluctuations around the Néel transition, in the magnetic susceptibility of pure Cr [20]. Thus in summary, in pure Cr there is a jump in the amplitude of the SDW at the Néel temperature, which produces a first-order change in the entropy [22] and the strain [23], with the possibility of such behaviour being obscured by other processes in the elastic moduli [24] and transport properties [25-27].

In the case of all physical properties except the susceptibility, however, doping with impurity atoms produces an apparently continuous transition at the Néel temperature in dilute alloys [3]. Often this may no doubt be attributed to smearing of the Néel transition because of non-uniformity of composition, but in the case of CrV alloys there is good evidence from the thermal expansion [23] and the neutron diffraction [16] that the V impurity induces a change from a first-order to a continuous transition. In the special case of a Cr+0.18 at.% Re alloy, the Néel transition remains first order [29], but this is believed to be due to the close proximity of the system to the phase boundary between the incommensurate and commensurate SDW phases.

Thus the behaviour of the magnetic susceptibility is anomalous. This is the only physical property that becomes discontinuous at the Néel temperature  $T_N$  in dilute alloys, while being continuous in pure Cr. The explanation may be quite simple, namely that when the SDW disappears at  $T_N$  a moment appears abruptly on the V impurity atoms, giving rise in a magnetic field to a jump in the magnetization and an apparent discontinuity in the

susceptibility. One might have expected to see similar behavior in alloys of Cr with Co [1, 2] and Mn [4], but perhaps sufficiently dilute alloys have not yet been measured, or else smearing of the Néel transition due to inhomogeneity of the samples obscured the effect.

The appearance of a moment on the V impurity atoms in dilute CrV alloys at the Néel transition may provide an explanation for the suppression of spin fluctuations in the paramagnetic phase. The evidence for such behaviour seen in the inelastic neutron scattering [15, 16] nuclear relaxation [30], and resistivity [31] has been reviewed by Fawcett [32].

#### 4. Conclusion

Local probes such as nuclear magnetic resonance, the Mössbauer effect, etc, whose use in Cr alloys to obtain microscopic information, including the existence of local moments, is reviewed in [3], should be employed to study dilute CrV alloys around the Néel transition. The present work encourages similar studies in other Cr alloy systems, especially those that have been observed to give rise to negative temperature dependence of the susceptibility in the paramagnetic phase (see table 5 in [3]).

Work is in progress [33] to explore details of the AC susceptibility near the magnetic phase transition. This should provide further insight into the nature of the transition.

The need is acute for theoretical consideration of the possible appearance of local moments in dilute Cr alloys, as occurs when transition metals are dissolved in other hosts [34], with the special feature that the moment is expected to disappear in most cases at the Néel transition. Any such analysis should also take cognizance of the existence of local impurity states in the energy gap of SDW systems. This concept was first introduced by Volkov and Tugushev [35], and experimental evidence for their existence in CrFe and CrSi alloys has been reviewed by Galkin [36]. It is evident that dilute Cr alloys provides a rich field for the study of magnetic impurity states.

#### Acknowledgments

This work was performed with the support of the Natural Sciences Research Council of Canada (EF and PC de C), the Fundacao de Amparo a Pesquisa do Estado de Sao Paulo and Superintendencia de Desenvolvimento Cientifico e Tecnologico (AJA de O, WAO and PC de C), and the Materials Technology Center at Southern Illinois University, Carbondale, IL (PH and NA).

#### References

- [1] Sukuki T and Takaki H 1964 *J. Phys. Soc. Japan* **19** 1241
- [2] Suzuki T 1966 *J. Phys. Soc. Japan* **21** 442
- [3] Fawcett E, Alberts H L, Galkin V Yu, Noakes D R and Yakhmi J V 1994 *Rev. Mod. Phys.* at press
- [4] Aidun R S, Arajs S and Moyer C A 1985 *Phys. Status Solidi b* **128** 133
- [5] Kondorskii E I, Kostina T I, Medvedchikov V P and Kuskova Yu P 1981 *Phys. Met. Metall.* **48** 27
- [6] Bender D and Müller J 1970 *Phys. Kondens. Materie* **10** 342
- [7] Arajs S, Kote G, Moyer C A, Kelly J R, Rao K V and Anderson E E 1976 *Phys. Status Solidi b* **74** K23
- [8] Booth J G 1966 *J. Phys. Chem. Solids* **27** 1639
- [9] Dadarlat D, Giurgiu A and Pop I 1980 *Solid State Commun.* **34** 109
- [10] Friedel J and Hedman L E 1978 *J. Physique* **39** 1225
- [11] Fawcett E and Galkin V Yu 1991 *J. Phys.: Condens. Matter* **3** 7167

- [12] Shibatani A, Motizuki K and Nagamiya T 1969 *Phys. Rev.* **177** 984
- [13] de Camargo P C and Brotzen F R 1982 *J. Magn. Magn. Mater.* **27** 65
- [14] de Camargo P C, Castro E P and Fawcett E 1988 *J. Phys. Met. Phys.* **18** L209
- [15] Noakes D R, Holden T M, Fawcett E and de Camargo P C 1990 *Phys. Rev. Lett.* **65** 369
- [16] Noakes D R, Holden T M and Fawcett E 1990 *J. Appl. Phys.* **67** 5262
- [17] Gelfuso V C and Ortiz W A to be published
- [18] Maxwell E 1965 *Rev. Sci. Instrum.* **36** 553
- [19] Laurent D G, Callaway J, Fry J L and Brener N E 1981 *Phys. Rev. B* **23** 4977
- [20] Hedman L 1993 private communication
- [21] Arrott A, Werner S A and Kendrick H 1965 *Phys. Rev. Lett.* **14** 1022
- [22] Williams I S, Gopal E S R and Street R 1979 *J. Phys. Met. Phys.* **9** 431
- [23] Fawcett E, Roberts R B, Day R and White G K 1986 *Europhys. Lett.* **1** 473
- [24] Muir W C, Perz J M and Fawcett E 1987 *J. Phys. Met. Phys.* **17** 2431
- [25] Muir W C and Strom-Olsen J O 1971 *Phys. Rev. B* **4** 988
- [26] Akiba C and Mitsui T 1972 *J. Phys. Soc. Japan* **32** 644
- [27] Fote A, Axler R, Schurmann H K and Mihalion T 1973 *Phys. Rev.* **138** 2099
- [28] Overhauser A W 1962 *Phys. Rev.* **128** 1437
- [29] Fawcett E and Noakes D R 1993 *Int. J. Mod. Phys. B* **7** 624
- [30] Kontani M and Masuda Y 1983 *J. Magn. Magn. Mater.* **31-34** 287
- [31] Vedernikov M V 1967 *Sov. Phys.-Solid State* **9** 2381
- [32] Fawcett E and Alberts H L 1992 *J. Phys.: Condens. Matter* **4** 613
- [33] de Oliveira A J A, de Camargo P C and Ortiz W A to be published
- [34] Heeger A J 1969 *Solid State Physics* vol 23 (New York: Academic) p 283
- [35] Volkov B A and Tugushev V V 1984 *Sov. Phys.-Solid State* **26** 147
- [36] Galkin V Yu 1993 *Int. J. Mod. Phys. B* **7** 638