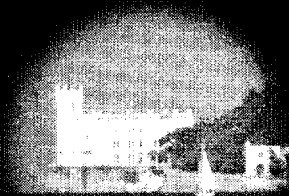


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**PHASE DIAGRAM OF $ZnCr_{2p}Al_{2-2p}S(Se)_4$
AND $Zn_{1-p}Cd_pCr_2S(Se)_4$**

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United Nations Educational Scientific and Cultural Organization
and
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Abstract

We compute the phase diagram of the nonmetallic compounds $\text{ZnCr}_{2p}\text{Al}_{12-2p}\text{S}(\text{Se})_4$ (I[S,Se]) and $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{S}(\text{Se})_4$ (II[S,Se]). We consider the bond-diluted Ising model on the spinel B site (S.B.S.) lattice with competitive exchange interactions, i.e. the ferromagnetic exchange interaction J_1 between nearest neighbours (n.n.) and the antiferromagnetic superexchange interaction J_2 between next-nearest neighbours' (n.n.n.) (and/or the more distant superexchange interactions J_i ($i > 1$)). Dilution and competition are found to be responsible for the spin glass phase and the percolation behaviour.

1. Introduction

The nature of the magnetic ordering in the series of pure chromium spinels is very sensitive to the distance between nearest-neighbouring (n.n.) Cr^{3+} ions and to the size of the anions [1-5]. The oxyspinels MgCr_2O_4 and ZnCr_2O_4 with a small Cr-Cr distance ($d_{\text{Cr-Cr}} = 2.94 \text{ \AA}$) order antiferromagnetically since the antiferromagnetic direct overlap of the d-orbitals for the n.n. is dominant. This contribution to interaction between n.n. J_1 decreases with the increase of the ion separation and may be overcome by the ferromagnetic superexchange via the anions leading to ferromagnetic order as in CdCr_2Se_4 ($d_{\text{Cr-Cr}} = 3.79 \text{ \AA}$). More distant superexchange interactions J_i ($i > 1$), which are less sensitive to the variation of the lattice parameter give rise to a helical ordering as in ZnCr_2Se_4 ($d_{\text{Cr-Cr}} = 3.71 \text{ \AA}$). As the Cr-Cr distance ($d_{\text{Cr-Cr}} = 3.53 \text{ \AA}$) in ZnCr_2S_4 is intermediate between that of the oxyspinel and the seleno compounds it may be argued that the set of relevant exchange integrals are just at the transition line between the helical and the commensurate structures.

Among these spinel compounds ZnCr_2S_4 is antiferromagnetic (AF) ($T_N = 18\text{K}$) [2,6], ZnCr_2Se_4 is AF ($T_N = 20\text{K}$) [3,7] and CdCr_2Se_4 is ferromagnetic (F) ($T_c = 128 \text{ K}$) [2,8] as CdCr_2Se_4 ($T_c = 84 \text{ K}$) [8].

However, it was recognised since the past two decades that quenched randomness may cause a fundamental change in the phase transition behaviour of solid state systems. For small randomness in the interactions, the effects are quite subtle; but, for systems with large randomness, especially with competing interactions, entirely new phenomena may occur. These include percolation effects, spin glass, and reentrant spin glass behaviour. Experiments on such systems with well-characterised, easily controllable

randomness played an important role in elucidating critical phenomena in the presence of quenched randomness.

This paper concerns the interesting topic of magnetic structure and spin glass behaviour in diluted B-spinel systems or spinel B-site (S.B.S.) lattices: $\text{ZnCr}_{2p}\text{Al}_{12-2p}\text{S}(\text{Se})_4$, where the disorder in the distribution of magnetic interactions is due to the dilution of the magnetic ion Cr and $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{S}(\text{Se})_4$ where the disorder is due to the substitution between diamagnetic ions ($\text{Zn}^{2+} \leftrightarrow \text{Cd}^{2+}$) on tetrahedral sites. The obtained theoretical phase diagrams are in rough qualitative agreement with the experimental ones.

2. Theory and Results

To study the critical phenomena in quenched random spin systems Sarbach 1980 [10] established a method based on evaluating the mean-field free energy. He applied the replica method to Ising simple cubic systems with quenched random interactions. The free energy of the mean field taking account of the randomness must be averaged overall configurations of the disorder, and in a straightforward way, is deduced by using the variational principle. This scheme gives the parameters one needs to characterise the magnetic phase diagram.

In this work we applied this procedure to three-dimensional bond-diluted S.B.S lattices $\text{ZnCr}_{2p}\text{Al}_{12-2p}\text{S}(\text{Se})_4$ (I[S,Se]) and $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{S}(\text{Se})_4$ (II[S,Se]) with competitive interactions. We use the Heisenberg Hamiltonian to compute the magnetic energy related to the exchange interactions. The interactions considered can be up to the fourth nearest neighbours bonds (according to the case and to the precision required) and

their exchange integrals are written down J_1, J_2, J_3 and J_4 . So, we consider the magnetic energy as a truncated sum of the pair contributions $S_i S_j$ of spins on sites i and j ,

$$H = \sum_{i,j} \sum_n J_{nij} S_i S_j$$

In fact, in the Hamiltonian we use, we take into account the specific geometry of the spinels; but we suppose a three-dimensional Ising spin $S = 1/2$ and introduce a magnetic field to provide an easy derivation of the susceptibility,

$$H = \sum_{i,j} \sum_n J_{nij} S_i S_j + \sum_j H_j S_j$$

where the coupling constants J_{nij} ($n=1, 2, \dots$) and the fields H_j are independent random variables with probability distributions $P(J_{nij})$ and $P(H_j)$, respectively. Due to the nature of the dilution (and substitution) problem we choose these distributions in the form

$$P(J_{nij}) = p\delta(J_{nij} - J_n) + (1-p)\delta(J_{nij} - J'_n)$$

$$P(H_j) = \delta(H_j - H)$$

where $(1-p)$ ($0 < p < 1$) is the dilution (or substitution) ratio. By the prime (') we differentiate between the exchange integrals of the two opposite pure compounds of the bond-random spinel system studied,

J_n for $\text{ZnCr}_2\text{S}(\text{Se})_4$ and $J'_n (=0)$ for $\text{ZnAl}_2\text{S}(\text{Se})_4$ in case I,

J_n for $\text{CdCr}_2\text{S}(\text{Se})_4$ and J'_n for $\text{ZnCr}_2\text{S}(\text{Se})_4$ in case II.

For zero or weak dilution ($0 \leq 1-p < 0.15$) it was determined experimentally that for system I a long-range helimagnetic order (H) builds up below the Néel temperature T_N

(which decreases in this interval in the case of $I[S]$ from 18 to 9 K), which order disappears for a lower value of p^* , but the transition to a spin glass (SG) phase remained unfathomable [11].

The obtained phase diagram of the diluted S.B.S. lattice in the whole range of the dilution for the systems $I[S,Se]$ is presented in Figure 1.a. and Figure 1.b. (solid lines). In figure 1.a. we have included, for comparison, the experimental results obtained by magnetic measurements given in Ref. [11]. The two lines, T_N and T_{SG} , associated to the P(paramagnetic)-H(helimagnetic) (represented in our work by a certain AF in the Ising case) and P(paramagnetic)-SG(spin glass) transitions, respectively, lightly shifted down as predicted, meet at the expected percolation value $p^* = 0.85$ for $I[S]$; however, the (reduced) coupling variables $J_1, J_2, J_3,$ and J_4 (1, -0.50, 0.20, 0.04) used are in the sequence expected +, -, +, + but slightly different from those deduced in [12] (1, -0.46, 0.12, 0.04). T_{SG} is slightly reentrant and the threshold of percolation is $p_c^* \cong 0.25$. This value is slightly different from that found by the Monte Carlo simulation [13]. From Fig. 1.a., one can find the properties already mentioned above, but one can also get more and new information concerning other properties.

In the case of $I[Se]$ (Fig. 1.b), where we use the (reduced) coupling variables $J_1, J_2, J_3,$ and J_4 as (1, -0.45, 0.15, 0.00) slightly different from those which can be deduced from [8,9], the two lines, T_N and T_{SG} , meet at the percolation value $p^* = 0.72$; and the threshold of percolation is $p_c^* \cong 0.22$. The order of frustration seems to be without effect on the threshold of percolation. However the value of p^* is clearly lowered, this is due to the switch of the J_4 . Therefore we can deduce the influence of this parameter.

In the system II, where the substitution concerns the diamagnetic ions, we cross the way between the opposite pure compounds $ZnCr_2S(Se)_4$ and $CdCr_2S(Se)_4$. So we cover

the intermediate situation between two different magnetic ion surroundings. We took just the interactions J_1 and J_2 (the other coupling variables are supposed to be zero) and represent the H phase, expected for lower values of p , by an AF in the Ising spin case. In the case of $\text{II}(\text{Se})$, we use the experimental values of the exchange constants $J_1=14.7\text{K}$; $J'_1=12.6\text{K}$; $J_2=-0.018 J_1$, and $J'_2=-0.087 J'_1$ (which are obtained on the basis of magnetic results combined with mean-field theory [14]).

The obtained phase diagram presented in Fig. 2.a (solid lines) has two tails, each one is "similar" to the last diagrams. The $p^*(\text{Zn})\approx 0.25$ and $p^*(\text{Cd})\approx 0.45$ limit three regions below the P area. The passage to the middle one (SG) is experimentally unfathomable. This phase corresponds to the frozen phase associated to a coexistence of two different surroundings of Cr; leading to special fluctuations of the signs and magnitudes of the superexchange interaction between the magnetic ions.

Such a magnetic system corresponds exactly to the "random bond" model, in contrast to the "classical" spin glass, whose magnetic ions are randomly located. From Fig. 2.a., one can see the good agreement between the theoretical phase diagram and experimental results obtained from magnetic measurements [15].

In the case of $\text{II}(\text{S})$, we use the experimental values of the exchange constants $J_1=11.8\text{K}$; $J'_1=1.6\text{K}$; $J_2=-0.028J_1$, and $J'_2=-0.055J'_1$ (which are deduced on the basis of the magnetic results [8]). The relevant modifications are the temperature values of the pure systems and mainly the move of the SG phase region (Fig. 2.b), which are a same to stay constant. This phase moves toward small p , such as $p^*(\text{Zn})\approx 0.2$ and $p^*(\text{Cd})\approx 0.4$. Indeed the frustration feature is more important in the ZnCr_2Se_4 system than the CdCr_2S_4 one; but the dilution of Zn by Cd in $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{Se}_4$ which increase the frustration of Cr causes this effect.

The regions A in figures 1.b (I [Se]) and 2.a (II [Se]), and B in figures 1.a (I [S]) and 2.b (II [S]) seem to be identical, i.e. the diamagnetic dilution (I) by Al and the cation substitution (II) by Cd, seem to induce the same magnetic behaviour. The magnetic moment of the Cr per spin is unchanged in the two cases. So, for small substitutions the common behaviour is due essentially to the change in the average value of the Cr-Cr distance.

To resume, we have estimated the phase diagrams of the three-dimensional spinel B-site lattice with two types of dilutions by means of the Sarbach method [10]. The results found are in rough qualitative agreement with the phase diagram of a number of real systems, and with the results of Monte Carlo simulations [13, 15 to 17]. In particular, they are in agreement with available experimental results on two particular S.B.S. [12,15]. Explicit conditions are obtained for the critical temperatures which agree with previous results for specific types of randomness [15, 18].

Acknowledgements

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References

- [1]R.P. VAN STAPELE, *Ferromagnetic Materials*, Vol. 3, Ed. E.P. WHOHLFARTH, North-Holland Publ. Co., Amsterdam 1982 (p. 603) and references therein.
- [2]N.MENYUK, K. DWIGHT, R. ARNOTT, and A.WOLD, *J. Appl. Phys.* 37, 1387 (1966).
- [3]F.K. LOTGERING, *Proc. Internat. Conf. Magnetism*, Nottingham, Institute of Physics and Phys. Soc., London 1964 (p. 533).
- [4]M. HAMEDOUN, A.WIEDENMANN, J.L. DORMANN, M. NOGUES, and J. ROSSAT-MIGNOD, *J. Phys. C* 19, 1783, 1801 (1986).
- [5]K. Afif, A. BENYOUSSEF, M. HAMEDOUN, A. HOURMATALLAH, *phys. stat. sol. (a)* 171, 571 (1999).
- [6]M. HAMEDOUN, A. RACHADI, A. HOURMATALLAH, D. EL ALLAM, and A. BENYOUSSEF, *phys. stat. sol. (b)* 191, 503 (1995).
- [7]R. PLUMIER, *C.R. Acad. Sci. Paris* 260, 3348 (1965).
- [8]P.K. BALTZER, M. ROBBINS, and P.J. WOJTOWICZ, *J. Appl. Phys.* 38, 953 (1967).
- [9]R. ABDELJALIL, Thesis, 8 June 1996, F.S. Fes Maroc.
- [10]S. SARBACH, *J. Phys. C* 13, 5033 (1980).
- [11]M. ALBA, H. HAMMANN, and M. NOGUES, *J. Phys. C* 15, 5441 (1982).
- [12]A. HOURMATALLAH, M. HAMEDOUN, A. RACHADI, and N. BENZAKOUR, *Physica B* 229, 256 (1997).
- [13]D. FIORANI, L. GASTALDI, A. LAPICCIRELA, S. VITICOLI, and N. TOMASSIMI, *Solid State Commun.* 32, 831 (1979).

- [14]M. HAMEDOUN, A. ZERHOUNI, A. RACHADI, M. SLIMANI, and A. BENYOUSSEF, phys. stat. sol. (b) 192,159 (1995).
- [15]H. MALETRA and W. FELSH, Phys. Rev. B 20, 1245 (1979).
- [16]K. BINDER, W. KINZEL, and D. STAUFFER, J. Phys. B 36, 161 (1979).
- [17]R. J. BIRGENEAU, R. A. COWLEY, G. SHIRANE, and H. YOSHIZAWA, J. Stat. Phys. 36, 817 (1984) and references therein.
- [18]S.F EDWARDS and P.W. ANDERSON, J. Phys. F 5, 965 (1975).

Captions

Fig. 1.a: Magnetic phase diagram of $\text{ZnCr}_{2p}\text{Al}_{12-2p}\text{S}_4$ [Fig. 1 of ref. 5]. The various phases are the paramagnetic phase (P), the antiferromagnetic phase (AF) and the spin glass phase (SG). The solid lines are the present results. The dots represent the experimental points deduced from the ac and dc susceptibility [10].

Fig. 1.b: Magnetic phase diagram of $\text{ZnCr}_{2p}\text{Al}_{12-2p}\text{Se}_4$. The solid lines are the present results. The dot represents the experimental temperature of the pure ZnCr_2Se_4 system [13].

Fig. 2.a: Magnetic phase diagram of $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{Se}_4$ [Fig. 2 of ref. 5]. The various phases are as the precedent figure plus the ferromagnetic phase (F). The solid lines are the present results. The dots represent the experimental points deduced from magnetic measurement [13].

Fig. 2.b: Magnetic phase diagram of $\text{Zn}_{1-p}\text{Cd}_p\text{Cr}_2\text{S}_4$. The solid lines are the present results. The dots represent the experimental temperature of the pure systems [8,13].

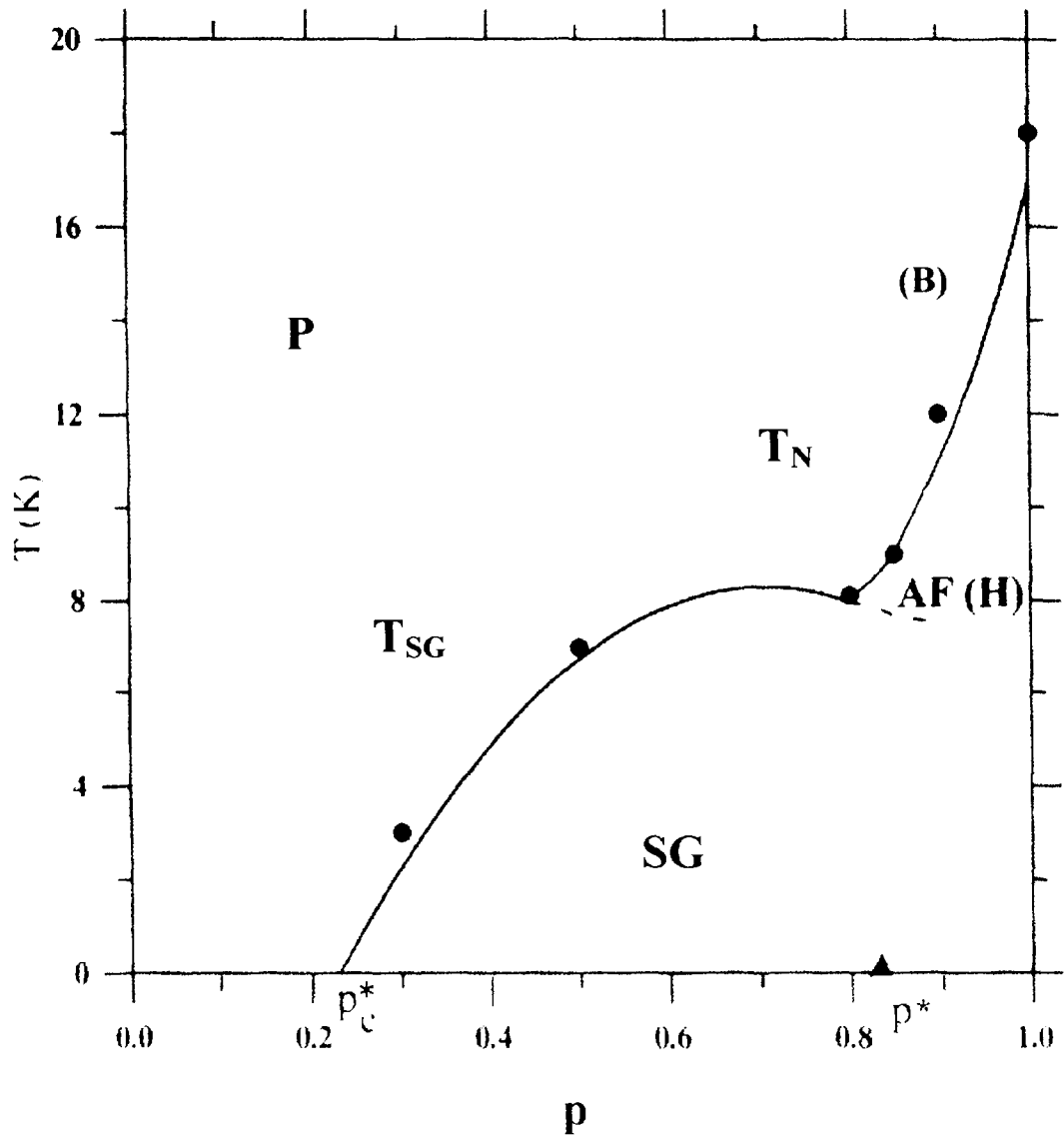


Figure 1.a

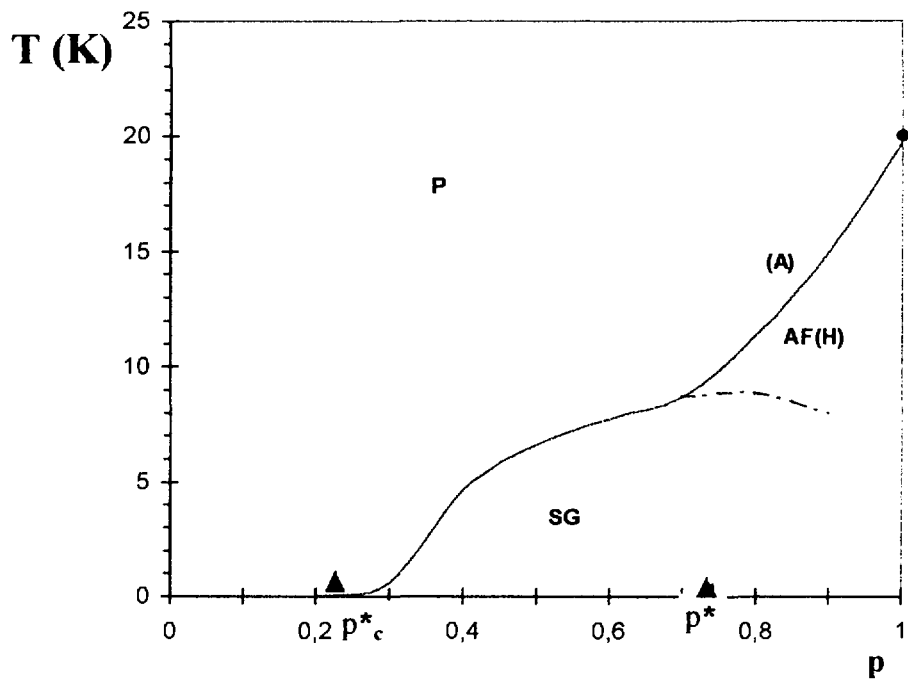


Figure 1.b

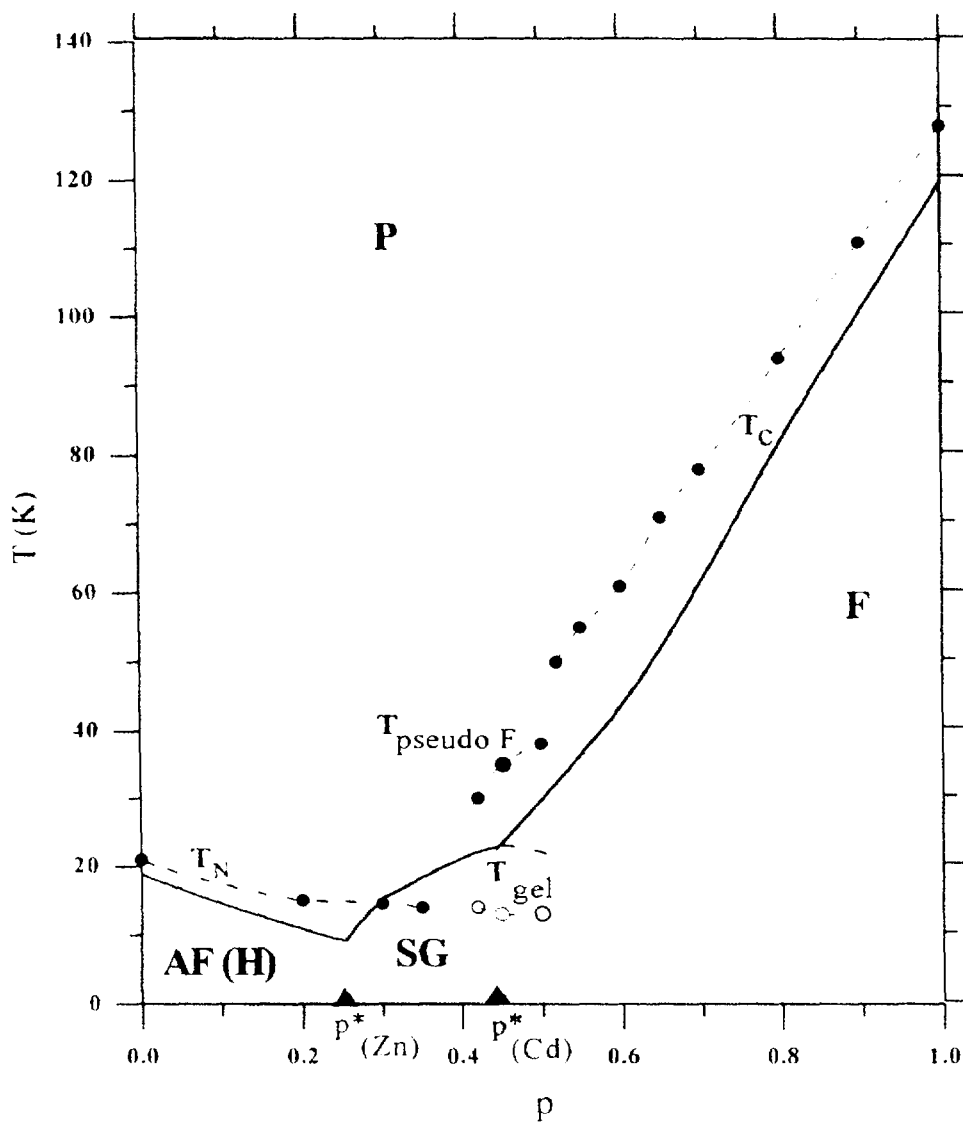


Figure 2.a.

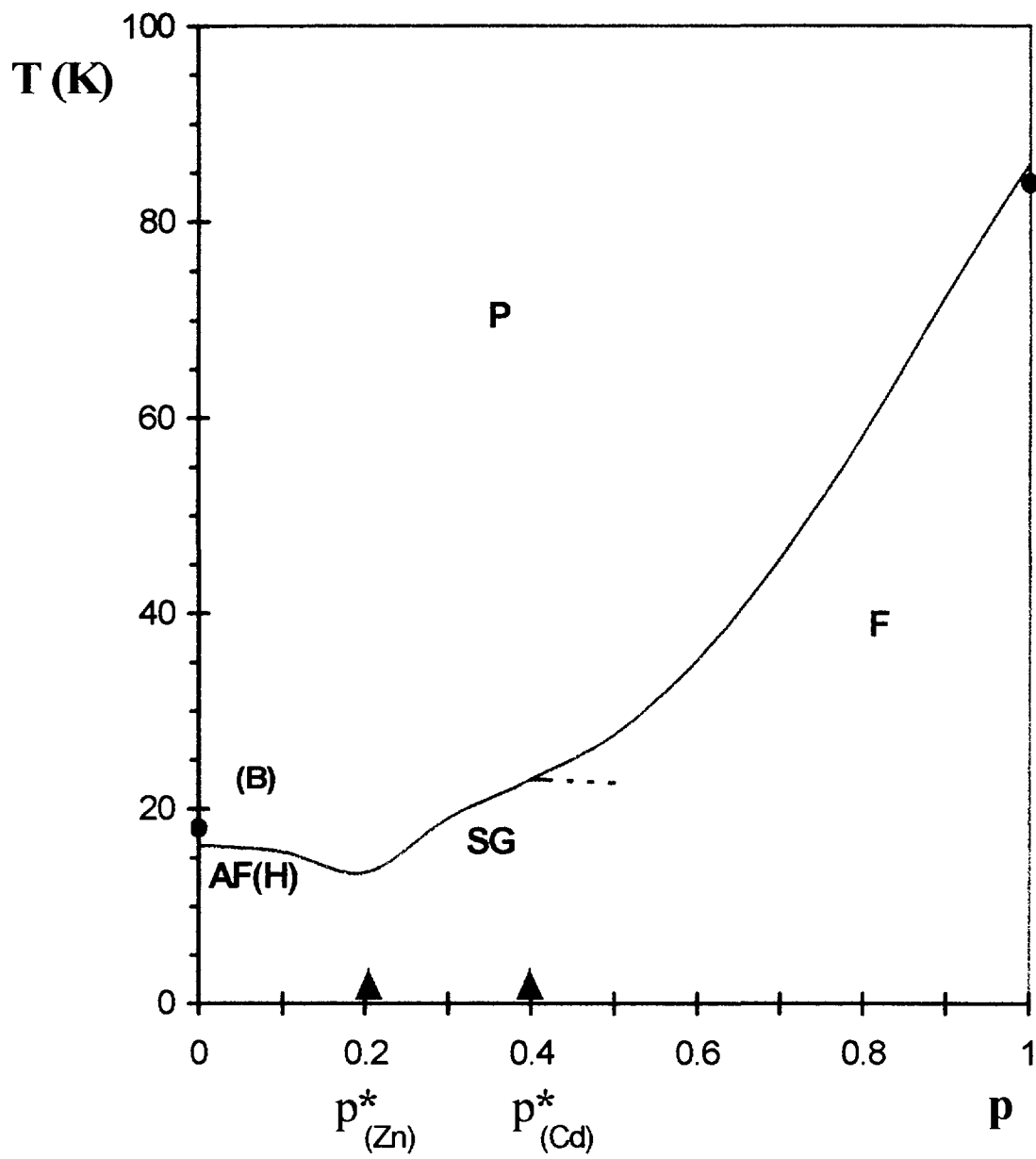


Figure 2.b