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INFLUENCE OF DILUTION AND NATURE OF THE INTERACTION
ON SURFACE AND INTERFACE MAGNETISM

by

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ABSTRACT

The recent theoretical effort of the Rio de Janeiro/CBPF group on surface magnetism is tutorially reviewed. Within a real space renormalization group framework, we analyze the influence of factors such as the number of states per spin (q -state Potts model), the signs of the coupling constants (mixed ferro and antiferromagnetic interactions), the presence of a second semi-infinite bulk (interface case), the symmetry of the interaction (anisotropic Heisenberg model), and surface and/or bulk dilution (bond quenched model). A variety of interesting physical effects emerges.

Key-words: Surface magnetism; Critical phenomena; Renormalization group.

I INTRODUCTION

During the last decade, surface magnetism has raised considerable interest both because of its various applications (catalysis, corrosion, etc.) and its intrinsic theoretical and experimental richness. Itinerant as well as localized ions magnetic systems have been studied. Nevertheless the field can be considered as being at its initial stage: this is due to the real experimental and theoretical difficulties associated with it.

Surface magnetic order has been experimentally exhibited on systems such as Ni, Cr, Gd [1-8]. On theoretical grounds, the problem has been treated within different frameworks, namely Mean Field Approximation [9-11], various Effective Field theories [12-15], Bethe Approximation [16], series expansion [17], Random Phase Approximation [18], Monte Carlo techniques [19], and Renormalization Group (RG) methods [20-30]. Several among these works (as well as others) have been reviewed by Binder [31]. We present here a comprehensive review of the theoretical effort [32-40] that has been very recently accomplished on the subject by the Rio de Janeiro/CBPF group and collaborators. We shall discuss, within the real space RG framework, the influence on the surface magnetism criticality (phase diagrams and universality classes) of the following factors: (a) the number of states per spin (q -state Potts model; Section III); (b) the signs of the coupling constants (mixed ferro and anti ferromagnetic interactions; Section IV); (c) the presence of a second semi-infinite bulk (interface case; Section V);

(d) the symmetry of the interaction (anisotropic Heisenberg model; Section VI); (e) surface and/or bulk dilution (bond quenched model; Section VII). To better understand the influence of all these factors, we shall first focus a prototype, which we choose to be the semi-infinite simple cubic spin 1/2 Ising ferromagnet with (1,0,0) free surface.

II PROTOTYPE

The Hamiltonian of our prototype is given by

$$H = - \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j \quad (\sigma_i = \pm 1, \forall i) \quad (1)$$

with $J_{ij} = J_S < 0$ if both i and j sites belong to the (1,0,0) surface, and $J_{ij} = J_B > 0$ otherwise. It is convenient to define $\Delta \equiv J_S/J_B - 1$.

The phase diagram of this system is known to be as given in Fig. 1. For $T < T_c^{3D} \equiv n^{3D} J_B/k_B$ (with $n^{3D} \simeq 4.511$) we have the bulk ferromagnetic (BF) phase, where both the bulk and the surface are magnetically ordered. For $T > T_c^{3D}$ the bulk is paramagnetic for all values of J_S/J_B , and the same happens with the surface if $\Delta \leq \Delta_c$ (with $\Delta_c \simeq 0.5 - 0.6$). But if $\Delta > \Delta_c$, an interesting intermediate surface ferromagnetic (SF) region appears where surface magnetic order exists, even if bulk order is absent. The SF phase emerges for T in the interval $(T_c^{3D}, T_c^S(\Delta))$ where, because the presence of the bulk enhances the correlations between surface spins, $T_c^S(\Delta) \geq T_c^{2D} \equiv$

$n^{2D} J_S / k_B$ (with $n^{2D} = 2.269\dots$); note that $T_c^S(\Delta_c) = T_c^{3D}$, and that necessarily $\Delta_c < n^{3D}/n^{2D} - 1$ (this general inequality implies, for the present model, $\Delta_c < 0.988$). For $T > T_c^S(\Delta)$, the entire system is in the paramagnetic (P) phase.

Let us say a few words on the magnetization (M) profile: if $\Delta \ll \Delta_c$ ($\Delta \gg \Delta_c$), M monotonously increases (decreases) from $M_S(T)$ (surface magnetization) to $M_B(T)$ (bulk magnetization) while going from the surface to deep in the bulk, and, if $\Delta \simeq \Delta_c$, M(T) presents a flat profile (M almost independent of the depth). In all cases, the bulk asymptotic value $M_B(T)$ is exponentially approached while coming from the surface. It is essentially this fact which explains why the criticality associated with the SF phase should be the 2D one (i.e., the system behaves as being an $\infty \times \infty$ finite one).

To illustrate the four different universality classes associated with the present system let us recall the thermal critical behaviour of M: (i) for all values of Δ , $M_B \propto (T_c^{3D} - T)^\beta$; (ii) for $\Delta < \Delta_c$, $M_S \propto (T_c^{3D} - T)^{\beta_1}$; (iii) for $\Delta = \Delta_c$ (SB multicritical point), $M_S \propto (T_c^{3D} - T)^{\beta^{SB}}$; (iv) for $\Delta > \Delta_c$, $M_S \propto (T_c^S(\Delta) - T)^{\beta^{2D}}$. We verify consequently the existence of four different critical exponents β . Finally, in the $\Delta - \Delta_c \rightarrow +0$ limit, we expect $T_c^S(\Delta)/T_c^{3D} - 1 \sim A(\Delta/\Delta_c - 1)^{1/\theta}$ which defines the crossover critical exponent θ and critical factor A.

Let us close this Section by adding that we expect a fifth non trivial singularity to be present in this problem for $\Delta > \Delta_c$, namely a soft singularity in $M_S(T)$ at $T = T_c^{3D}$ (when $M_B(T)$ vanishes): we are presently working out this point.

III RG APPROACH: POTTS MODEL

The real space RG approach we shall use along the present paper is illustrated here on the q -state Potts ferromagnet ($q=1$ and 2 respectively recover bond percolation and spin $1/2$ Ising model). The Hamiltonian is given by

$$\mathcal{H} = -q \sum_{\langle i,j \rangle} J_{ij} \delta_{\sigma_i, \sigma_j} \quad (\sigma_i = 1, 2, \dots, q, \forall i) \quad (2)$$

with $J_{ij} = J_S > 0$ if both i and j sites belong to the free surface, and $J_{ij} = J_B > 0$ otherwise; we introduce $K_{ij} \equiv J_{ij}/k_B T$.

The RG recursive relations are obtained by imposing

$$e^{-\mathcal{H}'_{12}/k_B T} = \text{Tr}_{3,4,\dots,N} e^{-\mathcal{H}_{12\dots N}/k_B T} \quad (3)$$

where \mathcal{H}'_{12} and $\mathcal{H}_{12\dots N}$ respectively denote the Hamiltonians associated with a (renormalized) single bond (2 sites) and a relatively large two-terminal cluster G (N sites). By imposing Eq. (3) we preserve all the equilibrium thermodynamical quantities as it implies the preservation of the partition function. Naturally we have to impose Eq. (3) twice: one to obtain $K'_B = f(K_B)$ (by using the bulk cluster G_B), and one to obtain $K'_S = g(K_S, K_B)$ (by using the surface cluster G_S). The choice of (G_B, G_S) determines the particular RG approximation. We have used two different choices, namely very simple clusters of the Migdal-Kadanoff type^[32] (qualitatively, but not always quantitatively, reliable as long as second order phase transitions are concerned; i.e.

roughly $q \leq 3$), and also recently introduced [33,41] clusters of a rather sophisticated shape (both qualitatively and quantitatively reliable for $q \leq 3$). We shall denote the first choice by $RG^{(1)}$ (it uses clusters noted $G_B^{(1)}$ and $G_S^{(1)}$: see Fig. 2 of Ref. [32]), and the second one by $RG^{(2)}$ (it uses clusters $G_B^{(2)}$ and $G_S^{(2)}$: see Figs. 2 and 3 of Ref. [33]).

The mathematical operations involved in Eq. (3) can in principle be performed through the traditional (though tedious!) inspection of all microscopic spin configurations. But we have used instead the Break-collapse method (BCM) [42-44] which very conveniently solves Eq. (3) through simple topological operations. In fact clusters such as those involved in $RG^{(2)}$ could hardly be solved, for arbitrary real value of q , were it not the BCM, as they yield polynomials of several thousands of terms. The knowledge of $f(K_B)$ and $g(K_S, K_B)$ closes the procedure as: (i) the RG flow in the (K_B, K_S) space determines the phase diagram as well as the universality classes, and (ii) the Jacobian $\partial(K_B', K_S')/\partial(K_B, K_S)$ at the relevant fixed points determines the values of the correlation length and crossover critical exponents (ν 's and ϕ respectively). The main results are indicated in Figs. 2 and 3. The calculation of the values of the various critical exponents β appearing in the problem involves the equations of states, and therefore a further step in complexity: we are presently working on that.

IV MIXED FERRO AND ANTIFERROMAGNETIC INTERACTIONS

Within the $RG^{(1)}$ framework we have studied [38] the in-

fluence, on criticality, of both signs for the q -state Potts coupling constants J_B and J_S . The situation described in Section III is herein recovered as the $J_B > 0$ and $J_S > 0$ particular case. The q -evolution of the phase diagram (in both t_B vs. t_S and T vs. J_S/J_B representations; see caption of Fig. 2 for definitions of t_B and t_S) and associated universality classes is depicted in Fig. 4. The well known ferro \leftrightarrow antiferro isomorphism in the simple cubic spin 1/2 Ising model is recovered for $q = 2$ (Figs. 4(c) and (d)). The phase diagram presents, besides the paramagnetic phase (P), various magnetic orders, namely the bulk ferromagnetic (BF; simultaneous surface ferromagnetic order), the bulk antiferromagnetic (BAF; simultaneous surface antiferromagnetic order), the surface ferromagnetic (SF, the bulk is disordered), the surface antiferromagnetic (SAF; the bulk is disordered), the simultaneous surface ferromagnetic and bulk antiferromagnetic (SF/BAF), and the simultaneous surface antiferromagnetic and bulk ferromagnetic (SAF/BF) ones. The various critical and multicritical fixed points determine the corresponding universality classes. In particular, the RG flow on the SF/BAF-BAF and SAF/BF-BF critical lines suggests first-order phase transitions. Further inspection is needed to clearly establish this possibility.

Note that while q increases, the SAF/BF phase disappears, then the SAF phase, and finally the SF/BAF and the BAF phases disappear as well. The disappearance of the SAF phase is already rigorously established [45] for $t_B = 0$: note however that the present RG approximation provides the disappearance at a value of q lower than it should ($q = 2.25$ instead of the exact [45] value 3). The q -evolution of the four multicritical

points ($J_B \neq 0$ or < 0 , $J_S > 0$ or < 0) is depicted in Fig. 5.

Let us finally address the most interesting phenomenon exhibited by this analysis, namely the existence, for $q \simeq 2$, of *re-entrances* in the phase diagram. This is to say, for negative J_S/J_B and within the appropriate range (which depends on q), we have, while increasing T , that the *surface* magnetic order vanishes at a relatively low temperature, and *reappears again below but close to the 3D critical temperature*, and finally vanishes again *above but close to the already mentioned 3D point*. In other words, the bulk order acts, on the surface one, somehow similarly to an uniform external magnetic field acting on a (highly anisotropic) antiferromagnet. Accordingly to the above facts, the surface order parameter should present a *maximum* in the neighbourhood (possibly *above*) of the 3D critical temperature: this is precisely what happens in Gd^[8]! Although we are not aware of any concrete arguments relating Gd to the $q \simeq 2$ Potts model, both experimental and theoretical facts are striking enough to suggest that in Gd *competitive signs* might exist between surface and bulk coupling constants.

V INTERFACE MODEL

The *free surface* case (bulk-surface-vacuum, with coupling constants J_B, J_S and 0 respectively) we have been discussing up to now can be generalized into the *interface* case (bulk 1-surface - bulk 2, with coupling constants J_1, J_S and J_2 respectively). Our calculations have been performed, within the

RG⁽²⁾ approach, for the (1,0,0) interface between two semi-infinite simple cubic lattices assuming ferromagnetic Potts interactions. The RG flow diagram is illustrated, for $q=2$, in Fig. 6; its $J_2/J_1 = 1/2$ section is represented, in the $(J_S/J_1, T)$ space, in Fig. 7. We now have *multicritical lines* (which include the previous *multicritical points*) which join in a *high-order multicritical point* (noted *equal bulk point*), in the neighbourhood of which a new type of crossover occurs. The parameter $\Delta_c \equiv \frac{J_S}{J_1} - 1$ (above which surface order is possible in the absence of bulk order) monotonously decreases when q and/or J_2/J_1 increase (see Fig. 8).

VI SYMMETRY OF THE INTERACTION

It is well known that the symmetry of the interaction is a very relevant ingredient of critical phenomena (e.g., it characterizes the universality class at a given dimensionality D). This is particularly true for $D=2$, where the Mermin-Wagner theorem forbids the existence of long range order at any finite temperature if the (short range) interaction is invariant under a *continuous* group of symmetry (e.g., isotropic Heisenberg and XY models, in opposition to the Ising model, which is related to a *discrete* group of symmetry). Let us also recall that the theorem says nothing about the existence of a phase transition: indeed, the $D=2$ XY model presents the well known Kosterlitz-Thouless phase transition, detectable through the divergence of the susceptibility. The Heisenberg model has a continuous group of symmetry which is *larger* than that of the

XY model, and consistently presents, at finite temperatures, no phase transition at all.

We go now back to the free surface (or even the interface) problem we are dealing with. Within the temperature interval where the SF phase exists, the magnetization profile is expected, as already said, to vanish exponentially while penetrating into the paramagnetic bulk (s). Its criticality is therefore expected to be that of the 2D system, and naturally all above considerations should hold. It is on these grounds that it becomes quite interesting the systematic analysis of the following spin 1/2 anisotropic Heisenberg Hamiltonian:

$$\mathcal{H} = - \sum_{\langle i,j \rangle} J_{ij} \left[(1 - \eta_{ij}) (\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y) + \sigma_i^z \sigma_j^z \right] \quad (3)$$

where (J_{ij}, η_{ij}) equals (J_S, η_S) if both i and j sites belong to the free surface, and equals (J_B, η_B) otherwise (note that $\eta_{ij} = 1, 0$ and $-\infty$ respectively correspond to the Ising, isotropic Heisenberg and isotropic XY models). The $J_B, J_S > 0, \eta_B = 1$ and $0 \leq \eta_S \leq 1$ models have been analyzed [34] within the RG⁽¹⁾ approach (the RG procedure which enables the treatment of quantum systems like the present one is described in Ref. [46]). The RG flow diagram and the η_S -dependence of Δ_c are respectively presented in Figs. 9 and 10(a). The extension to the interface problem ($J_2 \neq 0$ and $J_1 \equiv J_B$) has been discussed [37] as well: the results are depicted in Fig. 10. Δ_c monotonously increases when η_S and/or J_2/J_1 vary from 1 to 0. However it remains finite even for $\eta_S = J_2/J_1 = 0$: this is not in contradiction with the Mermin-Wagner theorem (or even with the fact that $T_c = 0$ for the $D = 2$ iso-

tropic Heisenberg model) because $\eta_B = 1$, and consequently *not* all the interactions present *continuous* group of symmetry. We are presently calculating [47] the influence of η_B , and will hopefully obtain $\lim_{\eta_B, \eta_S \rightarrow 0} \Delta_c = \infty$, consistently with the $D=2$ critical peculiarities.

VII BOND-DILUTE MODEL

Here we consider a different type of extension, namely quenched bond-dilution. The Potts ferromagnetic coupling constants for the interface problem will be assumed to be random variables with the following probability laws:

$$P_r(J_{ij}) = (1 - p_r) \delta(J_{ij}) + p_r \delta(J_{ij} - J_r) \quad (r = S, 1, 2) \quad (4)$$

The $p_S = p_1 = p_2 = 1$ particular case recovers the *pure* model we have been considering in Section V. The phase diagram of this quite general system involves hypersurfaces in a 6-dimensional parameter space, e.g., $(k_B T/J_1, J_S/J_1, J_2/J_1, p_S, p_1, p_2)$, the study of which is presently in progress. A few results within the $RG^{(1)}$ framework (bulk dilution in the $q=2$ free surface problem [36], interface dilution for arbitrary q [39], simultaneous interface and bulk dilution for arbitrary q [40], as well as within the $RG^{(2)}$ one (free surface dilution for arbitrary q [48]), are already available. Some interesting effects are depicted in Fig. 11 and 12. In particular we see in Fig. 11, that bulk dilution might be an excellent experimental manner for making

-11-

appear, at a given value of J_S/J_B (which is fixed for a given substance), surface magnetism.

VIII CONCLUSION

The influence of several factors on surface magnetism has been tutorially reviewed. Among those which present interesting effects and which might have strong relevance for experimental work, let us select the following ones: (i) ferro-antiferro competition between surface and bulk coupling constants; (ii) symmetry of the surface and bulk interactions; (iii) bulk dilution. Experimental evidence on these and other effects discussed here would be extremely welcome and enlightening.

CAPTION FOR FIGURES

Fig. 1 - Phase diagram of the spin 1/2 Ising ferromagnet in semi-infinite simple cubic lattice with (1,0,0) free surface (prototype model). The paramagnetic (P), bulk ferromagnetic (BF) and surface ferromagnetic (SF) phases join at the SB multicritical point (full-circle). The $\Delta \rightarrow \infty$ asymptotic straight line (dot-dashed) satisfies $k_B T/J_B = n^{2D} J_S/J_B$.

Fig. 2 - RG⁽²⁾ phase diagram for typical values of q ($t_r \equiv [1 - e^{-qK_r}] / [1 + (q-1)e^{-qK_r}]$, $r = B, S$). (a) Ising model: the RG flow is indicated; \blacksquare , \bullet and \circ respectively denote the trivial (fully stable), critical (semi-stable) and multicritical (fully unstable) fixed points. (b) Bond percolation: $p_r \equiv 1 - e^{-K_r}$ ($r = B, S$) according to the Fortuin and Kasteleyn theorem; the extrapolation procedure ("horizontal" stretching providing, by construction, the best values available in the literature for t_c^{3D}) is indicated as well; note that the semi-infinite bulk makes surface percolation possible below the 2D threshold $p_s = 0.5$. (c) Standard $k_B T/J_B$ vs. Δ representation.

Fig. 3 - q -evolution of Δ_c , A and ϕ (our best values [33]). For $q=2$, compare present Δ_c (0.569) with other available results: Mean Field Approximation [9,10] (MFA; 0.25), Effective Field Theory [15] (EFT; 0.4232), Bethe Approximation [16] (0.816), RG⁽¹⁾ [32] (0.736), series [17] (0.6 \pm 0.1), Monte Carlo [19] (MC; 0.50 \pm

0.03). For $q=2$, compare present ϕ (0.641) with other available results: ϵ -expansion [24] (\blacksquare ; 0.68) and MC [19] (\square ; 0.56 ± 0.04).

Fig. 4 - q -evolution of the phase diagram; $\tau \equiv \text{sign}(J_B)T/T_c$, T_c being the bulk Curie temperature. \blacksquare , \bullet and \circ respectively denote trivial, critical and multicritical fixed points. The dashed lines are indicative. $q=2$ has been indicated with more details as a prototype.

Fig. 5 - q -evolution of J_S^c/J_B (for $|J_S/J_B|$ above $|J_S^c/J_B|$ surface magnetic ordering can occur even in the absence of bulk ordering). For $q=2$, J_S^c/J_B equals 1.736 (compared to the series result [17] 1.60, and the Monte Carlo one [19] 1.50) and -2.28 (compared to the series result [17] -1.9). For the simple cubic lattice, the present RG cannot be retained much above $q=3$ as the bulk transitions will become of the first order.

Fig. 6 - $q=2$ RG⁽²⁾ flux diagram; \blacksquare , \bullet and \circ respectively denote fully stable (trivial), semistable (critical and multicritical) and fully unstable (high-order multicritical) fixed points. The five possible phases are indicated: the two single-bulk ferromagnetic (BF_1 and BF_2), the double-bulk ferromagnetic (BF_{12}), the surface ferromagnetic (SF) and the paramagnetic (P) ones.

Fig. 7 - RG⁽²⁾ q -evolution of the phase-diagram for $J_2/J_1=0.5$.

Fig. 8 - RG⁽²⁾ q -evolution of Δ_c for typical ratios J_2/J_1 ($J_2/J_1=0$ and 1 respectively correspond to the free surface and equal bulks cases).

- Fig. 9 - RG⁽¹⁾ flux diagram for the free surface anisotropic Heisenberg on Ising bulk ferromagnet ($t_r \equiv \tanh K_r$, $r = B, S$); $\eta_S = 1$ corresponds to the Ising model.
- Fig. 10 - RG⁽¹⁾ dependence of Δ_c on η_S and J_2/J_1 , for the interface anisotropic Heisenberg between two Ising bulks; $\eta_S = 1$ corresponds to the Ising model. (a) For $J_2/J_1 = 0$; (b) for typical values of η_S .
- Fig. 11 - Free surface Ising RG⁽¹⁾ p_B -evolution of the phase diagram (a) and the localization J_S^c/J_B of the multicritical point (b).
- Fig. 12 - Free surface Ising RG⁽²⁾ p_S -evolution of the phase diagram. Note the existence of the SF phase *below* the 2D percolation threshold $p_g = 1/2$; it disappears at $p_S = 0.415 \pm 0.003$.

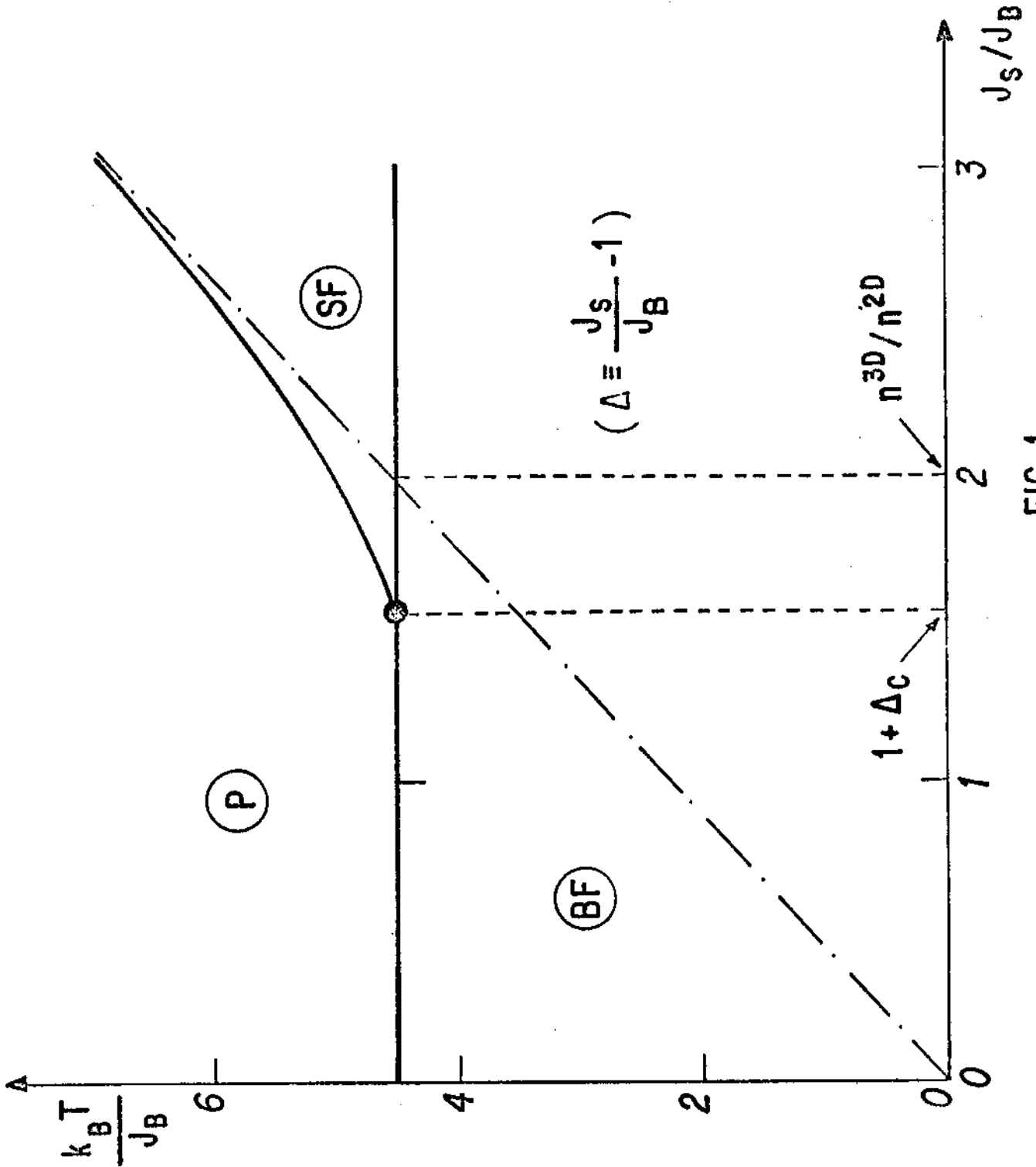


FIG. 1

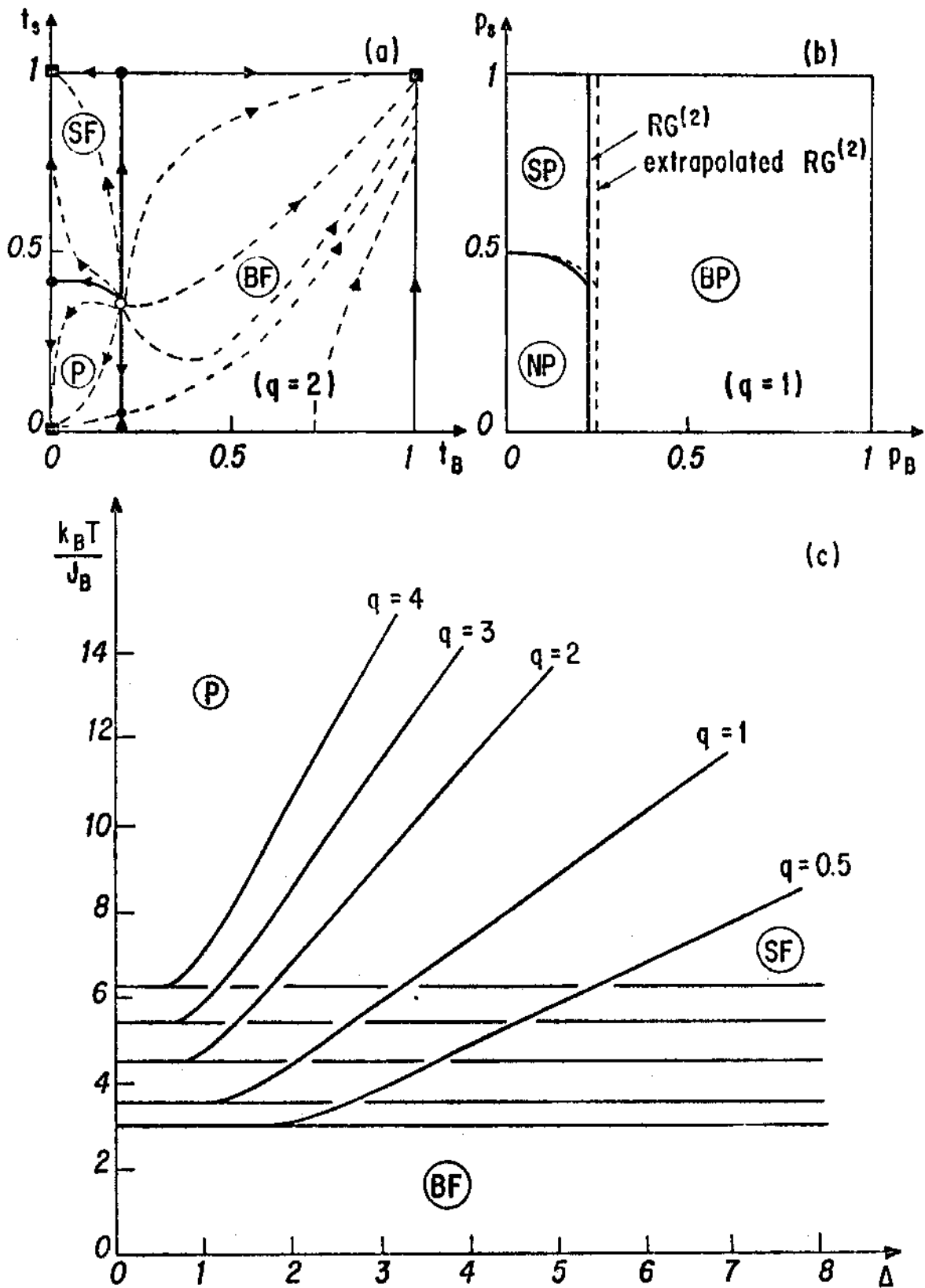


FIG. 2

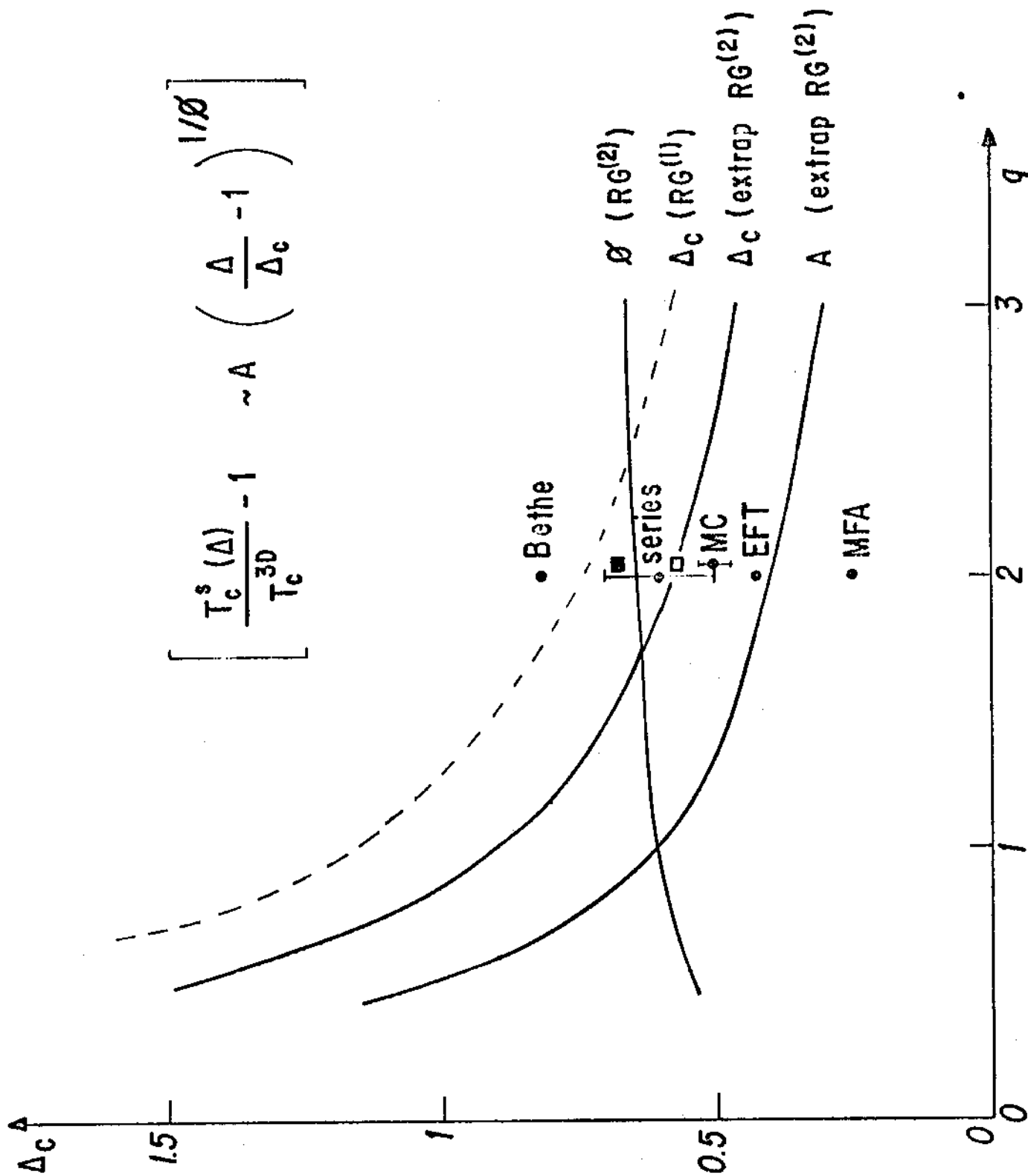


FIG. 3

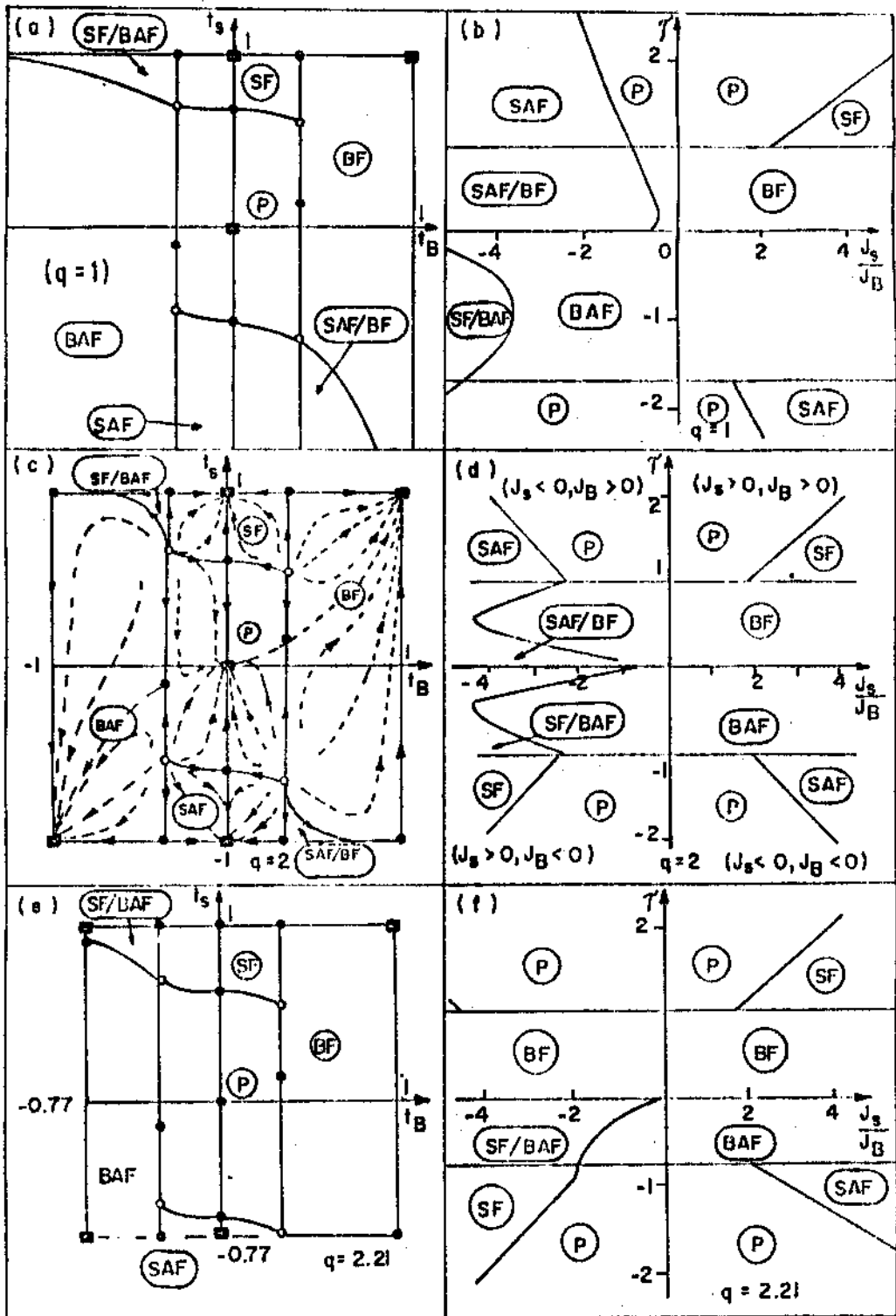


FIG. 4

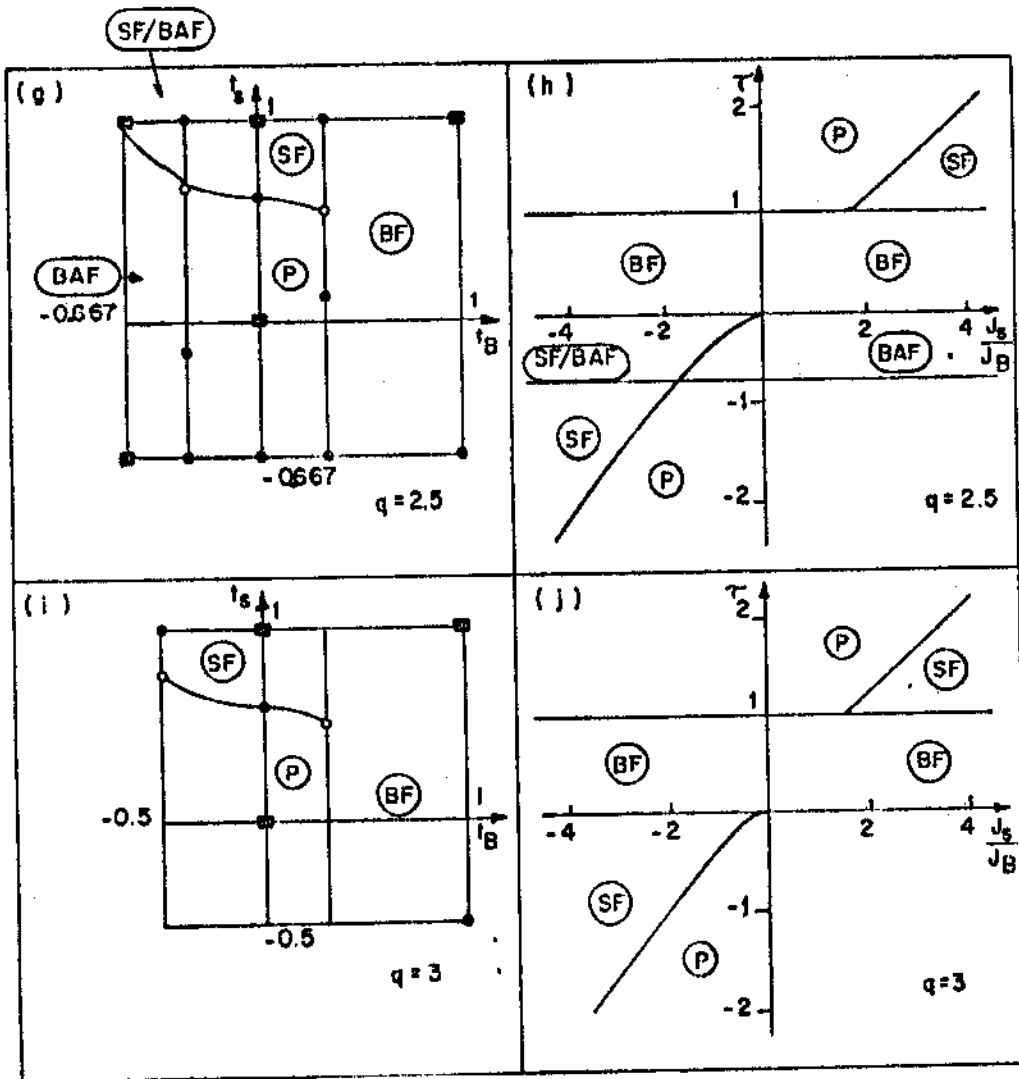


FIG. 4 (continued)

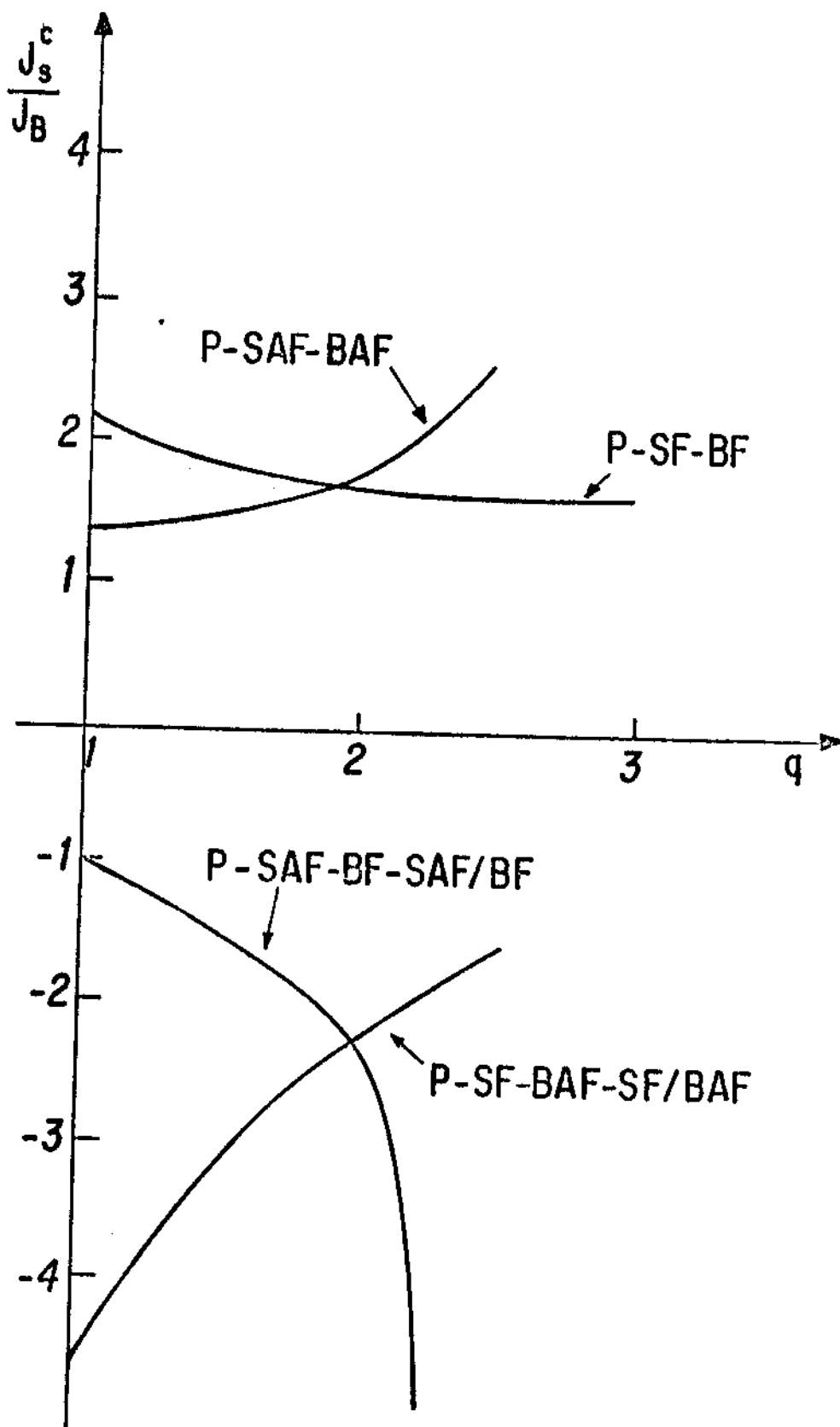


FIG.5

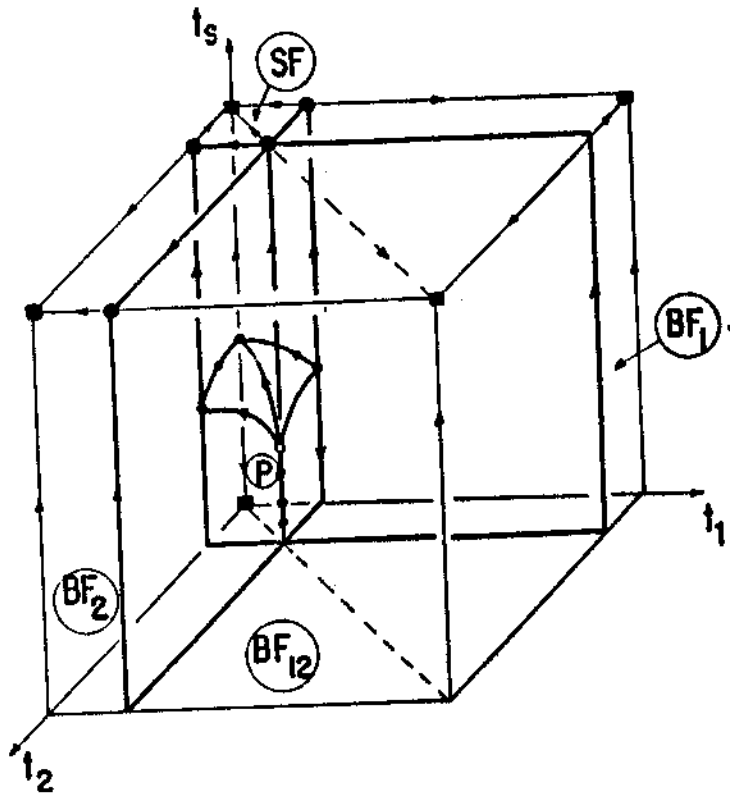


FIG. 6

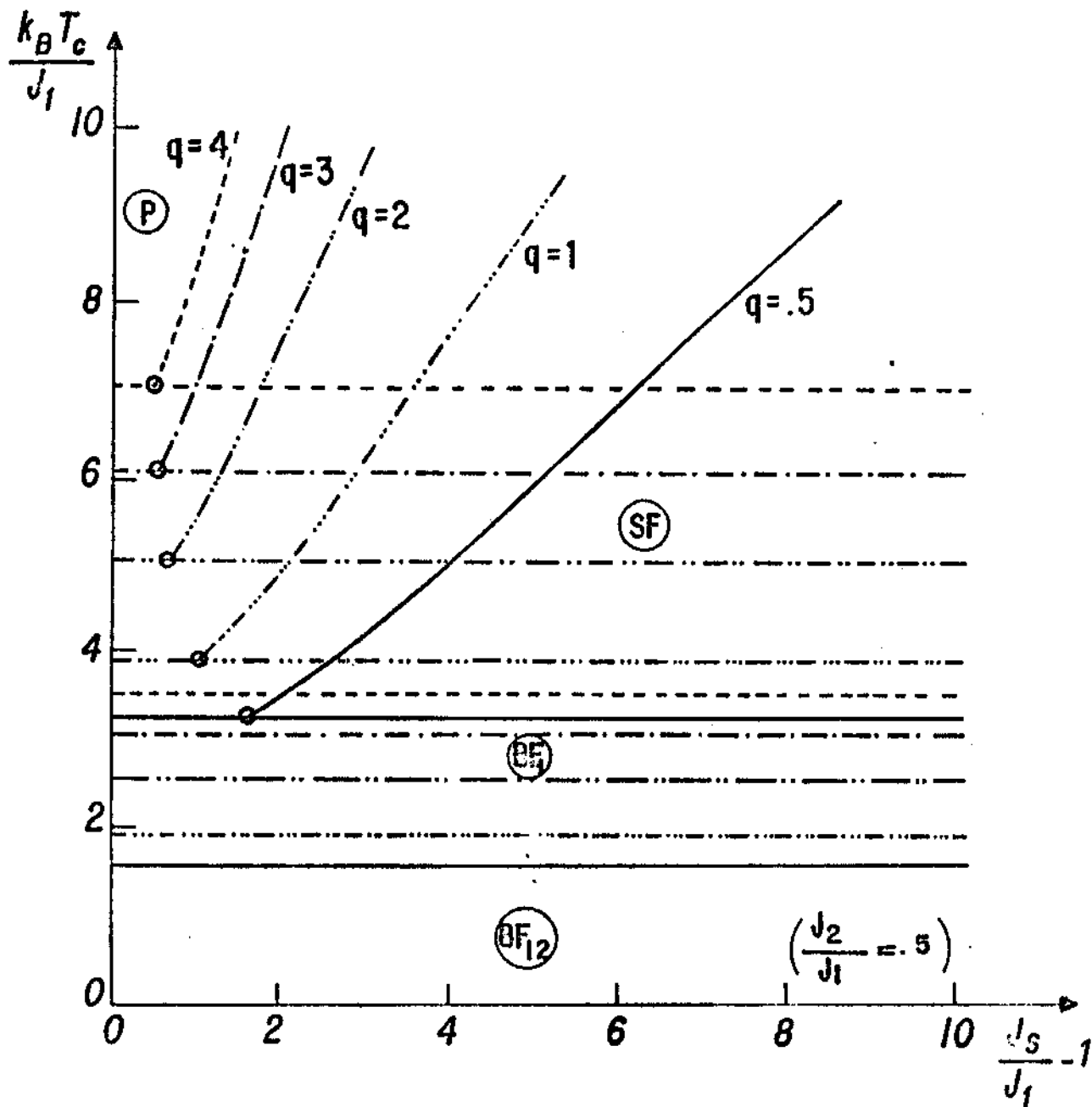


FIG. 7

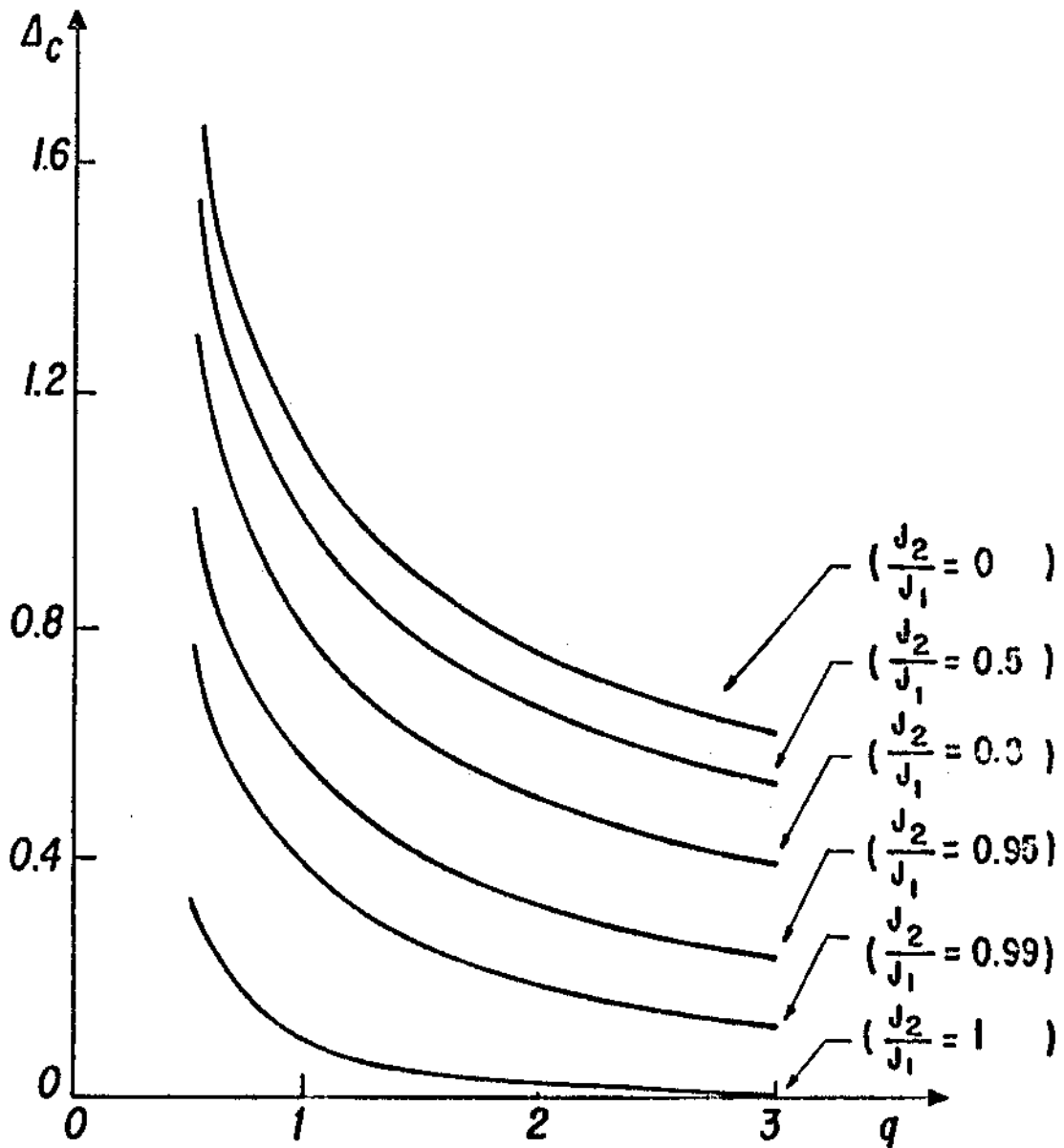


FIG. 8

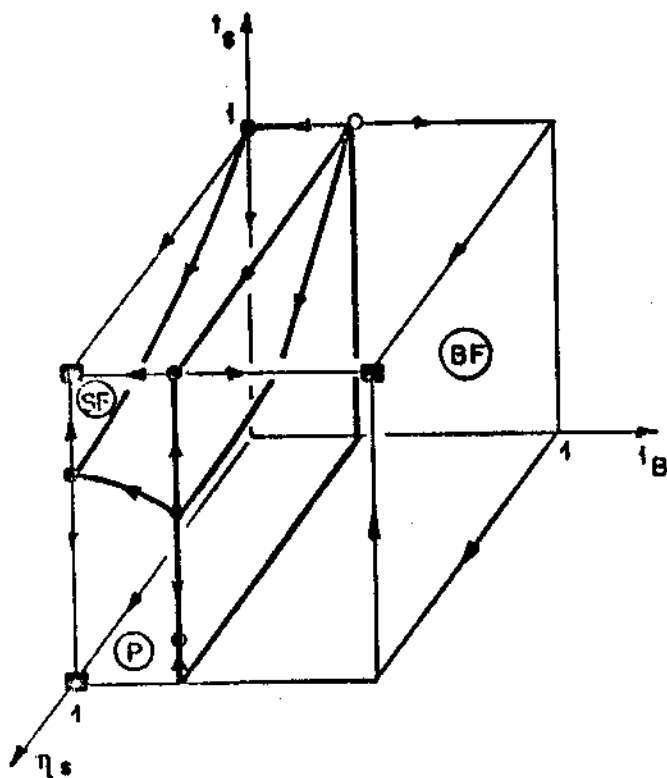


FIG. 9

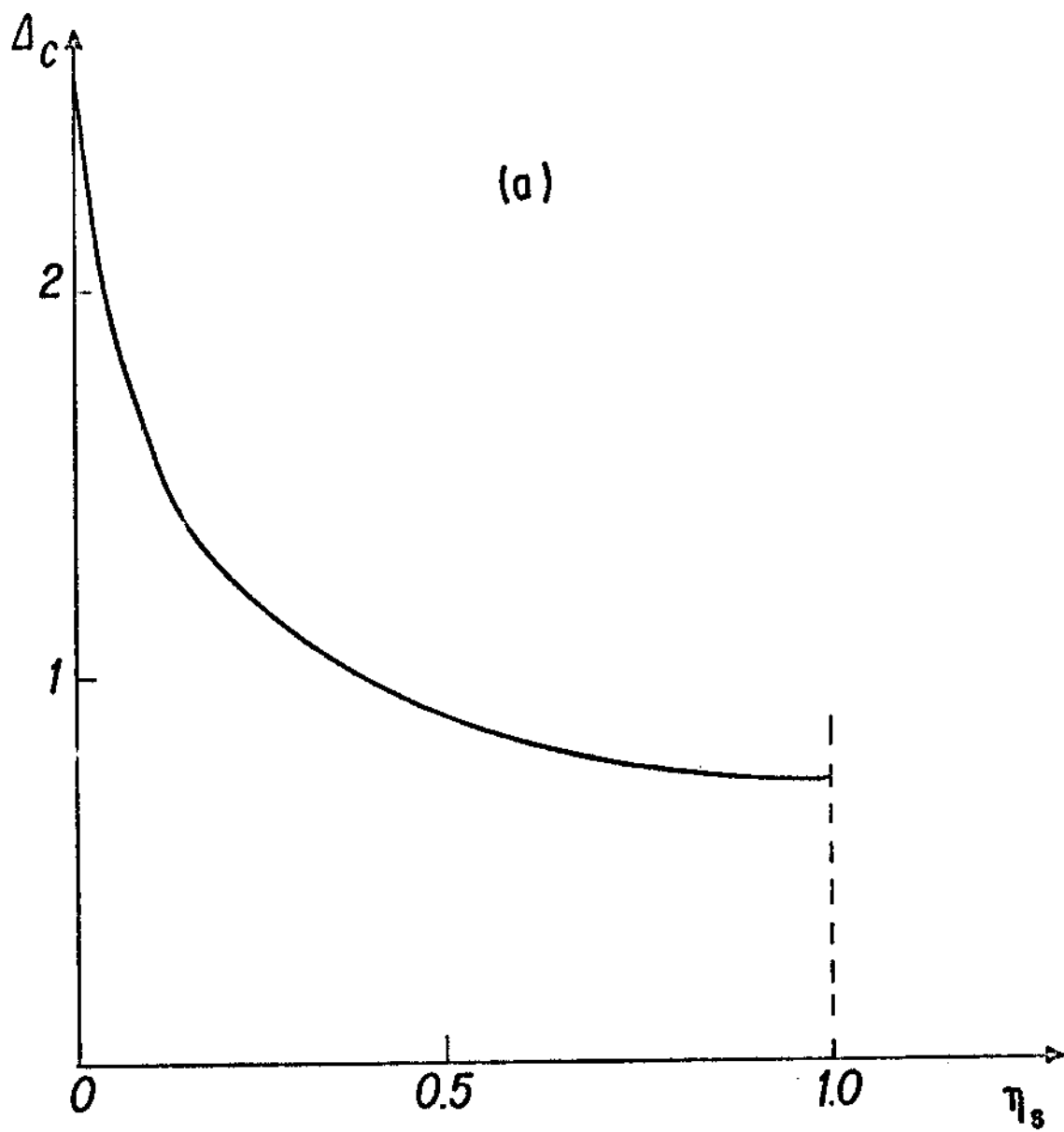


FIG.10

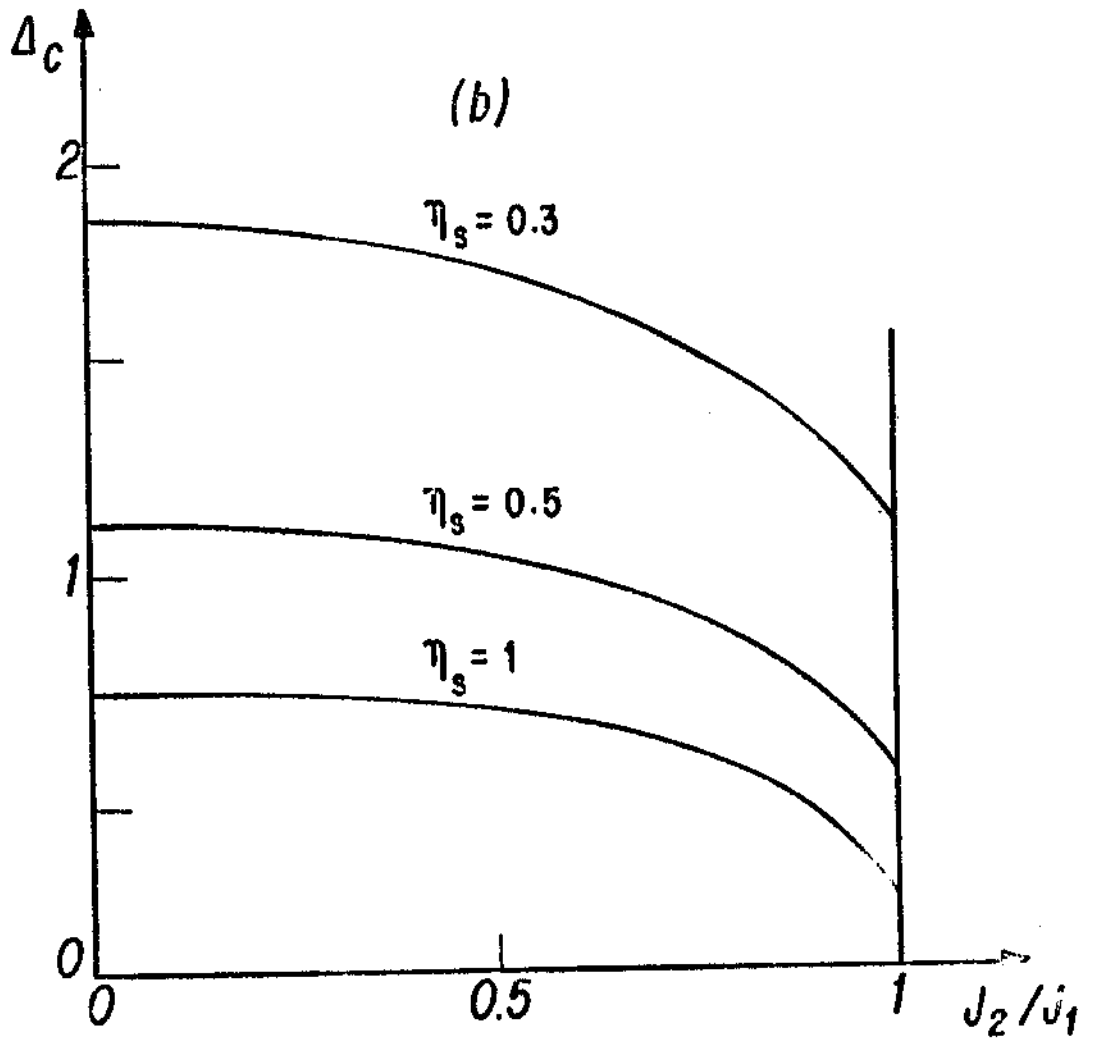


FIG. 10

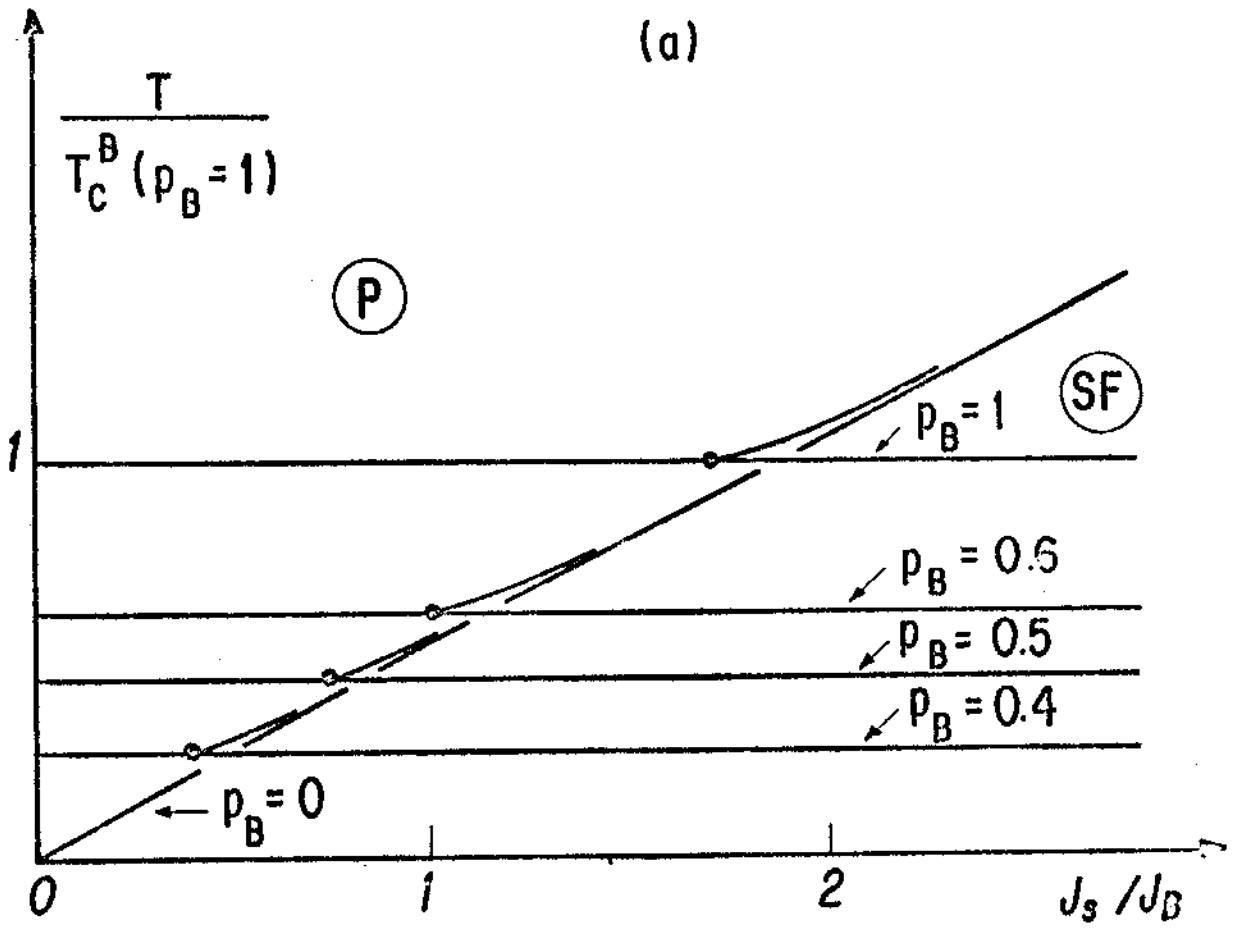


FIG. 11

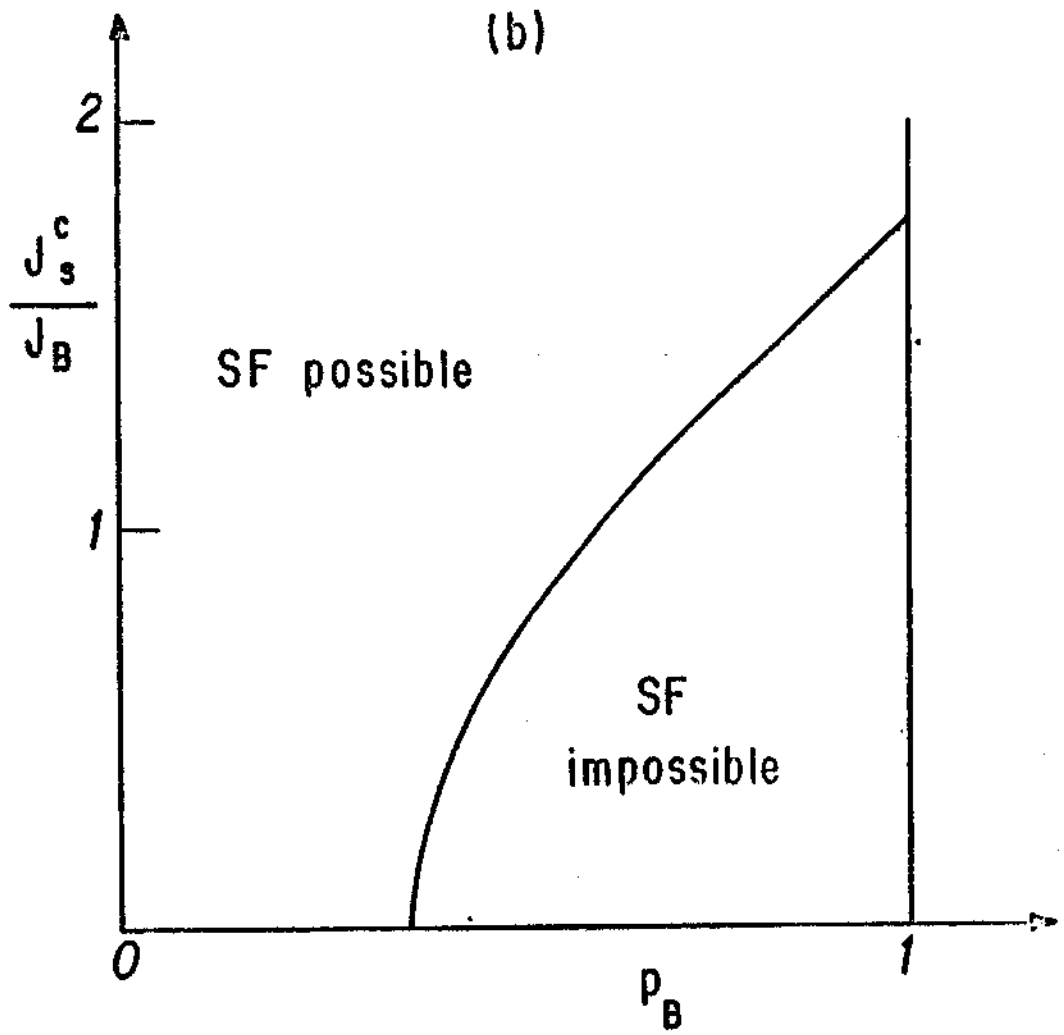


FIG.11

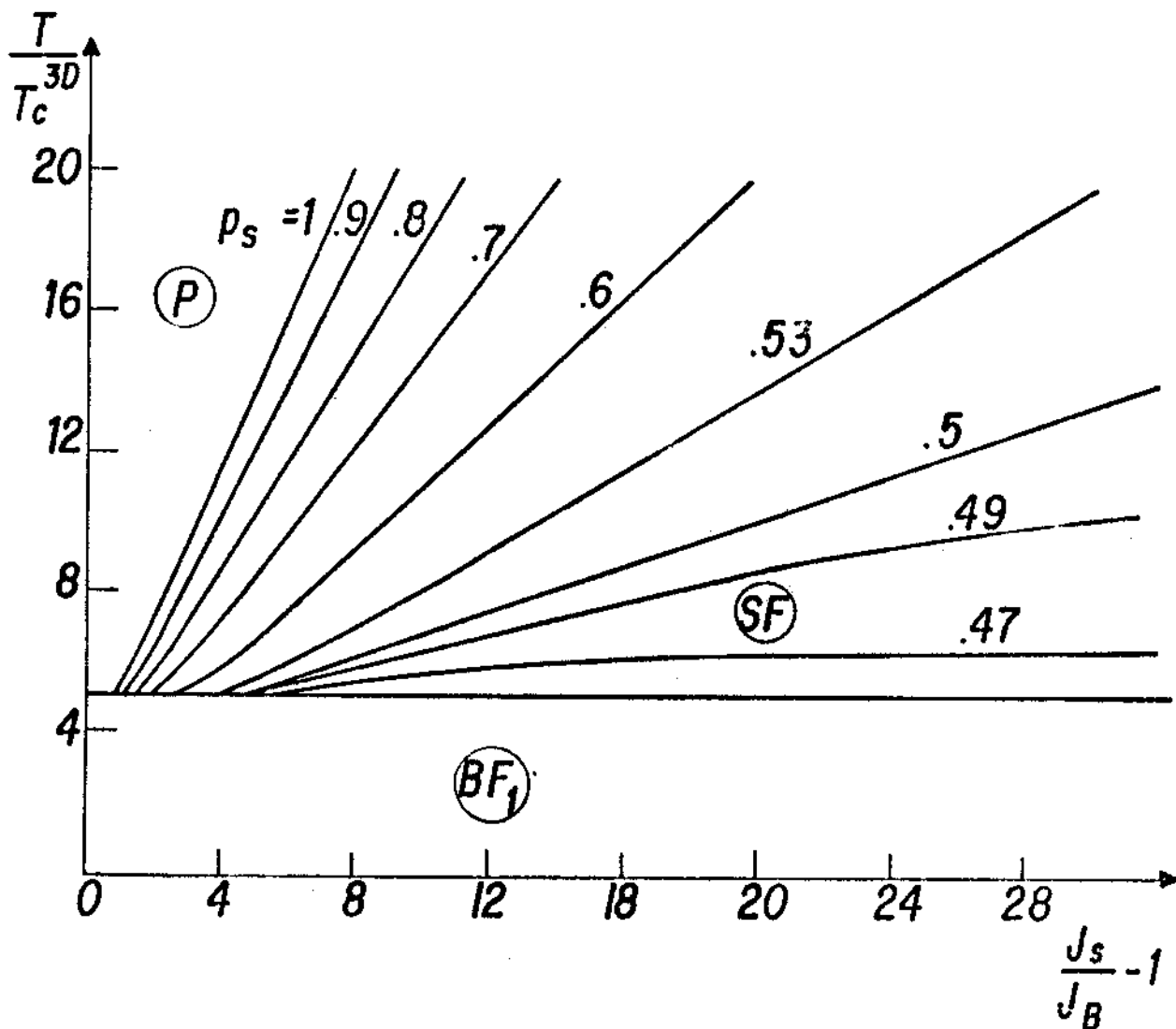


FIG.12

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