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MAGNETISM OF SINGLET-SINGLET IONS COUPLED TO ITINERANT ELECTRONS: APPLICATION TO Pr Fe_2

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Short title: Magnetism of Singlet-Singlet Ions: Pr Fe_2

Abstract

The combined role of crystal field, intraband and electron-ion exchange in determining the magnetic behaviour of a system composed of singlet-singlet localized ions and conduction electrons is investigated. A parametric study of the model is performed for the temperature dependence of electronic and ionic magnetisations, inverse-susceptibilities and magnetic specific heats. An application of the model for the case of Pr Fe_2 is performed in relation to the temperature dependence of magnetisation.

Key-words: Pr Fe_2; Crystal field; Electron-ion exchange; Intraband exchange; Magnetisation; Susceptibility; Magnetic specific heat.

I. Introduction

The magnetism of the heavy rare-earth intermetallics, like RFe_2 (R = heavy rare-earth), involves two kinds of magnetic moments: one associated to the magnetic moment of 4f electrons of the rare-earth, the other due to the band splitting of the d-conduction electrons. As a first approximation one may assume that the relevant exchanges are the electron-ion exchange and the intraband exchange [1]. In the case of light rare-earth intermetallics, due to the large radii of 4f-electrons, one expects that the description of the localized magnetic moment may be affected by crystal field effects. Actually, in analysing anisotropic magnetic quantities a proper combination of exchange interaction and crystal field effects is the usual approach even in the case of heavy rare-earth intermetallics, like $HoA\ell_2$, studied by Sankar et al. [2].

In this paper we study a simple model in which the crystal field effects are reduced to two singlet levels. These splitted f-sublevels ions interact by exchange with conduction electrons. We derive several magnetic quantities and perform a parametric study of the model, concentrating on the effects of intraband exchange interaction. An application of our results to the temperature dependence of the magnetization of Pr Fe_2, obtained by Shimotomai et al. [3], allow us to estimate typical values for the parameters of the model.

The paper is organized as follows. In section II, we introduce the model Hamiltonian and the magnetic quantities to be computed; in section III we present the magnetic state equations, obtained in the mean field approximation, the equi-T_c expression and the electronic and ionic magnetic specific heats. In section IV, we perform a parametric study of the model and finally, section V, we apply this study to the available magnetic data of Pr Fe_2.

II. Model Hamiltonian

The system consisting of conduction electrons and ions, coupled by electron-ion exchange, in the presence of an external magnetic field is described by

$$H = H_{e\ell} + H_{ion} + H_{exch} + H_{magn} \tag{1}$$

where

$$H_{e\ell} = \sum_{ij\sigma} T_{ij} C^+_{i\sigma} C_{j\sigma} + \frac{I}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} \tag{2}$$

$$H_{ion} = - \Delta \sum_i S_i^x \tag{3}$$

$$H_{exch} = - 2J \sum_i S_i^z s_i^z \tag{4}$$

$$H_{magn} = - 2g_i \alpha \mu_B h \sum_i S_i^z - g_e \mu_B h \sum_i s_i^z \tag{5}$$

where Δ is the crystal field energy (difference between the first excited and ground state levels); J is the electron-ion exchange and I the intraband exchange; T_{ij} is the kinetic energy in the Wannier representation; $C^{+}_{i\sigma}$ and $C_{i\sigma}$ are the creation and annihilation operators ($\sigma = \uparrow$ or $\downarrow$) in the Wannier representation; $n_{i\sigma} = C^{+}_{i\sigma}C_{i\sigma}$ and $s^{z}_{i} = \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})$; g_i and g_e are the Landé's factors for the ionic and electronic spins; α is the matrix element of the angular momentum of the ion between excited and ground states, supposed to be singlet states; S^{x}_{i} and S^{z}_{i} are pseudo spins associated to the two level singlet-singlet ion [4]; μ_B and h are the Bohr magneton and the external magnetic field.

We are essentially interested in the following magnetic quantities.

1. The temperature dependence of the electronic and the ionic magnetisations and the corresponding inverse magnetic susceptibilities as a function of the parameters of the model;
2. The Curie temperature as a function of the parameters of the model;
3. The electronic and ionic magnetic specific heats versus temperature.

III. Magnetic State Equations, Curie Temperature and Specific Heats.

In what follows we adopt the mean field approximation: the ions (electrons) feel an effective field created by the electronic (ionic) system. This leads (see Appendix) to two effective Hamiltonians

$$\tilde{H}_{ion} = H_{ion} - 2\, g_i \alpha \mu_B h_{ion} \sum_i S^{z}_{i} \qquad (6\text{-a})$$

$$\tilde{H}_e = H_{kin} - g_e \mu_B h_{e\ell} \sum_i s_i^z \tag{6-b}$$

where

$$h_{ion} = \frac{J\langle s^z\rangle}{2g_i \alpha \mu_B} + h \tag{7-a}$$

$$h_{e\ell} = \frac{2I\langle S^z\rangle}{\mu_B g_e} + \frac{J\langle S^z\rangle}{\mu_B g_e} + h \tag{7-b}$$

From equations 6-a and 7-a one obtains [4]

$$2\langle S^z\rangle = \frac{J\xi + 4g_i \alpha \mu_B h}{\left[(J\xi + 4g_i \alpha\mu_B h)^2 + 4\Delta^2\right]^{\frac{1}{2}}} \tanh \frac{\left[(J\xi + 4g_i\alpha\mu_B h)^2 + 4\Delta^2\right]^{\frac{1}{2}}}{4k_B T} \tag{8}$$

From 6-b and 7-b one obtains,

$$\int_{-\infty}^{\infty} d\varepsilon\, n(\varepsilon) \left[f(\varepsilon + \mu_B H_e) - f(\varepsilon - \mu_B H_e)\right] = zN\xi \tag{9-a}$$

$$\int_{-\infty}^{\infty} d\varepsilon\, n(\varepsilon) \left[f(\varepsilon + \mu_B H_e) + f(\varepsilon - \mu_B H_e)\right] = zN \tag{9-b}$$

where $n(\varepsilon)$ is the energy band density of states per spin; $f(x)$ is the Fermi distribution function, which depends on temperature and on the chemical potential $\mu(h_{e\ell}, T)$; z is the number of electrons per band; N is the number of electrons in the crystal and $\xi = 2\langle s^z\rangle$.

At this point we adopt the narrow band limit, i. e, $n(\varepsilon) = \frac{N\delta}{2}(\varepsilon - \varepsilon_0)$ and put $z=1/2$ (half filled band). The equations 9 then become

$$\xi = \frac{1}{e^{\beta(\varepsilon_0+\mu_B h_{e\ell}-\mu)}+1} - \frac{1}{e^{\beta(\varepsilon_0-\mu_B h_{e\ell}-\mu)}+1} \qquad (10\text{-a})$$

$$1 = \frac{1}{e^{\beta(\varepsilon_0+\mu_B h_{e\ell}-\mu)}+1} + \frac{1}{e^{\beta(\varepsilon_0-\mu_B h_{e\ell}-\mu)}+1} \qquad (10\text{-b})$$

which have the following solution

$$\mu = \varepsilon_0 \qquad (11\text{-a})$$

$$\xi = \tanh \frac{\mu_B h_e}{2k_B T} \qquad (11\text{-b})$$

using 7-b, 11-b becomes

$$\xi = \tanh \frac{I\xi + J\langle S^z\rangle + 2\mu_B h}{4k_B T} \qquad (12)$$

The equations 8 and 12 are the desired magnetic state equations, from which one gets the temperature dependence of the ionic and electronic magnetisations and inverse susceptibilities for a given set of model parameters I, J and Δ.

From 8 and 12, for $h = 0$, one obtains, taking the limit $\xi \to 0$, $\langle S^z\rangle \to 0$, for $T \to T_c$, the equi-T_c equation

$$4\left(\frac{k_B T_c}{I}\right) = 1 + \frac{\left(\frac{J}{I}\right)^2}{4\frac{\Delta}{I}} \tanh \left(\frac{\frac{\Delta}{I}}{\frac{2k_B T_c}{I}}\right) \qquad (13)$$

The expressions for ionic and electronic inverse-susceptibilities, for $T > T_c$, can also be derived from equations 8 and 12,

$$\frac{\mu_B h}{\xi\Delta} = \frac{8(\frac{k_B T}{\Delta}) - \frac{1}{2}(\frac{J}{\Delta})^2 \tanh(\frac{\Delta}{2k_B T}) - \frac{2I}{\Delta}}{2\,\frac{J}{\Delta}\, g_i\alpha \tanh\frac{\Delta}{2k_B T} + 4} \tag{14-a}$$

$$\frac{\mu_B h}{2<S^z>\Delta} = \frac{8(\frac{k_B T}{\Delta}) - \frac{1}{2}(\frac{J}{\Delta})^2 \tanh\frac{\Delta}{2k_B T} - \frac{2I}{\Delta}}{\left[2g_i\alpha(8\frac{k_B T}{\Delta} - \frac{2I}{\Delta}) + \frac{2J}{\Delta}\right]\tanh\frac{\Delta}{2k_B T}} \tag{14-b}$$

Finally, the ionic and electronic magnetic specific heats, for $h = 0$, may be easily obtained,

$$C_H^{(i)} = \frac{(J\xi)^2 + 4\Delta^2}{16k_B T^2}\,\mathrm{sech}^2\left\{\frac{\left[(J\xi)^2 + 4\Delta^2\right]^{\frac{1}{2}}}{4k_B T}\right\} \tag{15-a}$$

$$C_H^{(e)} = \frac{(J<S^z> + I\xi)^2}{4k_B T^2}\,\mathrm{sech}^2\left(\frac{J<S^z> + I\xi}{4k_B T}\right) \tag{15-b}$$

Expression 15-a was obtained in reference 4; (15-b) is derived from the Helmholtz free energy

$$\Omega = -K_B T\int_{-\infty}^{\infty} d\varepsilon n(\varepsilon)\left\{\ell n(1+\exp[\beta(\mu-\varepsilon-\mu_B h_{e\ell})]) + \ell n(1+\exp[\beta(\mu-\varepsilon+\mu_B h_{e\ell})])\right\} \tag{16}$$

in the narrow band limit and using (7-b).

In the next section we make a parametric study of the temperature dependence of magnetisations, inverse-susceptibilities and magnetic specific heats, putting emphasis on the role of intraband interaction.

IV. Parametric Behavior of the Model

Figures 1-a, 1-b and 1-c show the temperature dependence of electronic, ionic and total magnetisations and inverse susceptibilities for $\frac{I}{\Delta} = 0.0$ and $\frac{J}{\Delta} = 1.0$, 2.0 and 10.0. These results display the role of $\frac{J}{\Delta}$ in the absence of electron-electron interaction.

Figures 2-a, 2-b and 2-c show the same quantities referred in Figures 1-a, 1-b and 1-c, but for $\frac{J}{\Delta} = 2.0$ and $\frac{I}{\Delta} = 0.0$; 4.0 and 8.0. A comparison between these figures show that for increasing values of $\frac{I}{\Delta}$ one increases the values of T_c and changes dramatically the temperature dependence of the magnetisations and inverse-susceptibilities; the magnetisations at $T = 0$ are not sensitive to changes in $\frac{I}{\Delta}$.

Figures 3-a, 3-b and 3-c show the electronic, ionic and total magnetic specific heats versus temperature for $J = 2.0$ and $\frac{I}{\Delta} = 0.0$; 4.0 and 8.0. The total specific heat of figure 3-c show a complex structure which can be analysed in terms of the partial contributions of the ionic and electronic counterparts. In figure 3-a, one notes that the maximum height of the electronic specific heat does not change with $\frac{I}{\Delta}$. In figure 3-b, both the heights and widths of the curves depend on $\frac{I}{\Delta}$; in constrast to figure 3-a, the ionic specific heat does not go to zero above T_c.

V. Application to Pr Fe_2

The magnetism of Pr Fe_2 has been studied by Shimotomai et al. [3]

using the Mössbauer effect and the measurement of the saturation magnetisation. Further studies on Pr Fe_2 were also performed by Meyer et al. [5] in comparison with $NdFe_2$ and YFe_2.

We have taken the hyperfine field measurements versus temperature data from Shimotomai et al. [3] between 193K and 390K, and have assumed a linear dependence between $H_{eff}(T)$ and M(T), the proportionality constant being obtained from $H_{eff}(0)$ = 181 koe and $M(0) = 4.7\mu_B$. These data are shown in figure 4. The solid curve is obtained fitting the total magnetisation, obtained from (8) and (12), $\frac{M}{\mu_B} = \xi + 2g_i\alpha<S^z>$. Taking $\Delta = 2.5$ mev, the fitting is obtained for $g_i\alpha = 3.5$; J = 205.0 mev and I = 64.0 mev . The derived Curie temperature is 525K.

The model here proposed, despite the crudness of the narrow-band limit, allow us to obtain a fair agreement of the temperature dependence of the magnetisation in terms of crystal field, electron-ion exchange and electron-electron interaction; it also suggests what one would expect from magnetic susceptibility and magnetic specific heat measurements.

Appendix

In order to derive (6), with h_{ion} and $h_{e\ell}$ defined in (7), we adopted the following approximation

$$\sum_i S_i^z s_i^z \cong \frac{1}{2} \langle S^z \rangle \sum_i s_i^z + \frac{1}{2} \langle s^z \rangle \sum_i S_i^z \qquad (A.1)$$

$$\mathcal{H}_{exch} \cong - J \langle s^z \rangle \sum_i S_i^z - J \langle S^z \rangle \sum_i s_i^z \qquad (A.2)$$

$$\mathcal{H}_{exch} + \mathcal{H}_{magn} = - 2 g_i \alpha \mu_B \left(\frac{J \langle s^3 \rangle}{2 g_i \mu_B} + h \right) \sum_i S_i^z -$$

$$- g_e \mu_B \left(\frac{J \langle S^3 \rangle}{g_e \mu_B} + h \right) \sum_i s_i^z \qquad (A.3)$$

$$\sum_i n_{i\uparrow} n_{i\downarrow} \cong \frac{1}{2} \langle n_\uparrow \rangle \sum_i n_{i\downarrow} + \frac{1}{2} \langle n_\downarrow \rangle \sum_i n_{i\uparrow}$$

$$= - 2 \langle s^z \rangle \sum_i s_i^z + \frac{1}{2} \sum_i (\langle n_\uparrow \rangle n_{i\uparrow} + \langle n_\downarrow \rangle n_{i\downarrow}) \qquad (A.4)$$

$$I \sum_i n_{i\uparrow} n_{i\downarrow} \cong - g_e \mu_B \left(\frac{2 I \langle s^z \rangle}{g_e \mu_B} \right) \sum_i s_i^z \qquad (A.5)$$

The last term in A4, commutes with $\mathcal{H}_{kin}$ and s_i^z, and so is not included in A5.

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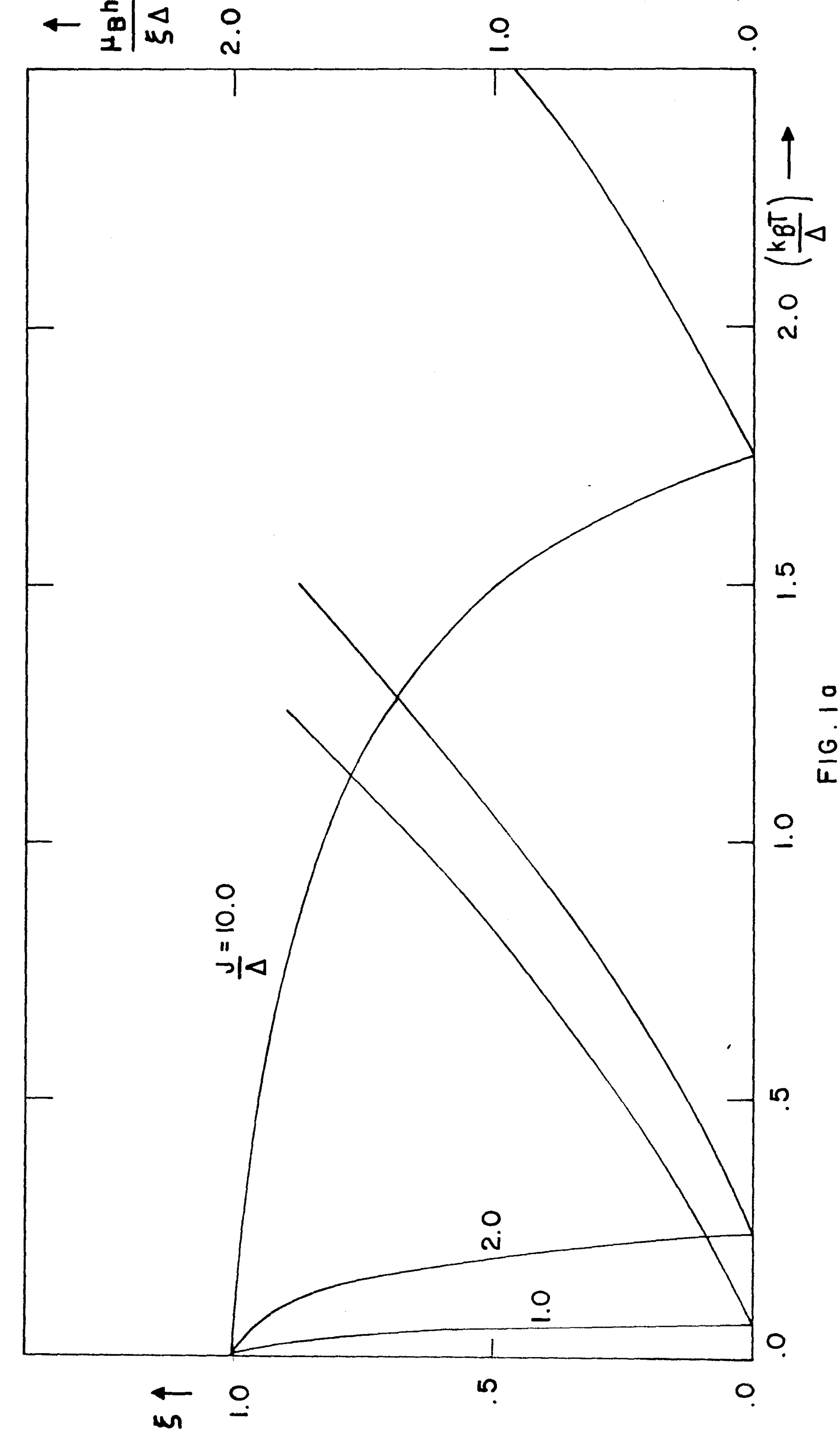
Figure Captions

Fig. 1a, 1b and 1c - Temperature dependence of electronic, ionic, and total magnetisations and inverse-susceptibilities for $I/\Delta = 0.0$ and $J/\Delta = 1.0$; 2.0 and 10.0.

Fig. 2a, 2b and 2c - Temperature dependence of electronic, ionic, and total magnetisations and inverse-susceptibilities for $J/\Delta = 2.0$ and $I/\Delta = 0.0$; 4.0 and 8.0.

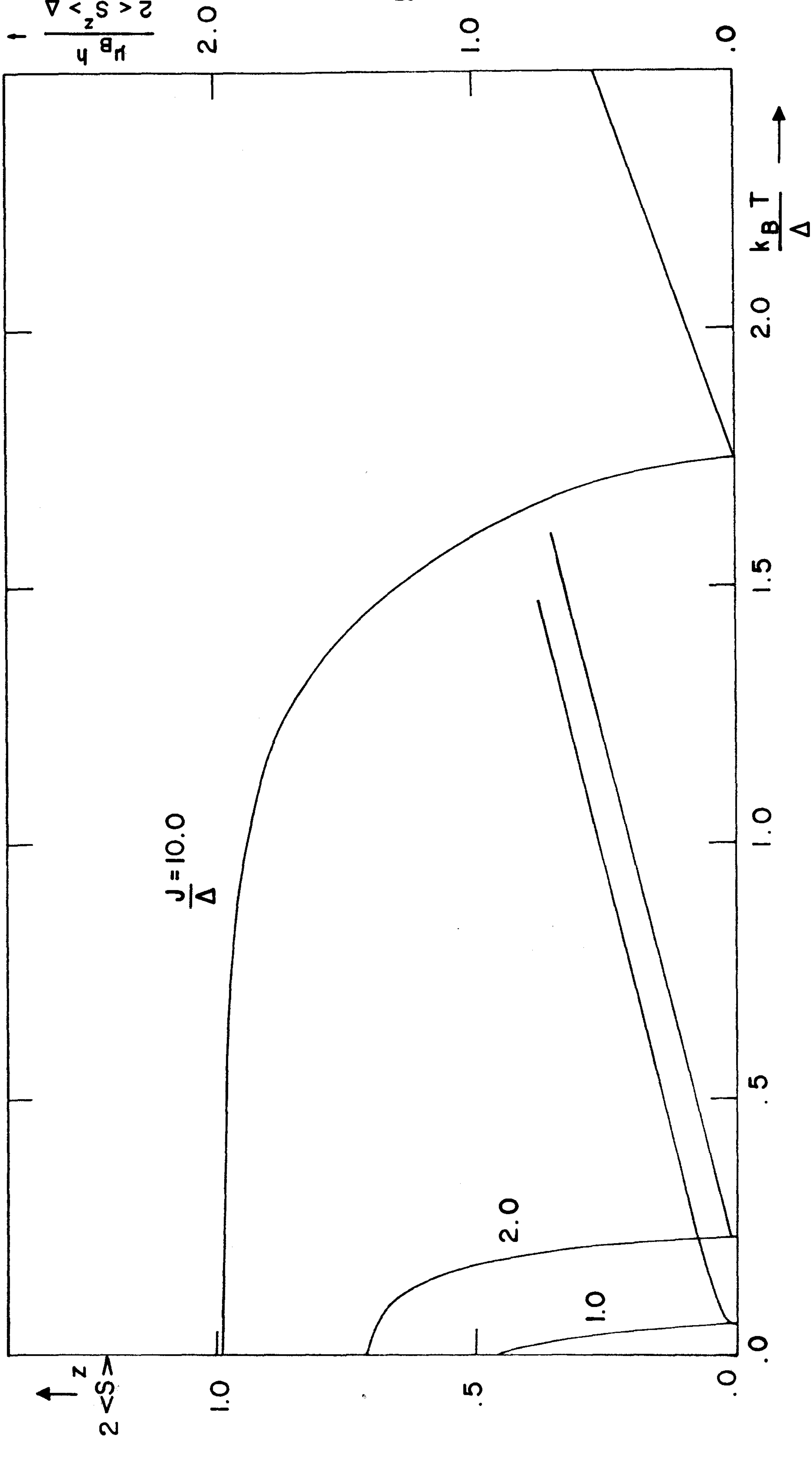
Fig. 3a, 3b and 3c - Temperature dependence of electronic, ionic, and total magnetic specif heats for $J/\Delta = 2.0$ and $I/\Delta = 0.0$; 4.0 and 8.0.

Fig. 4 - Temperature dependence of magnetisation using Shimotomai et al. measurements. The solid curve is theoretically calculated.



$\frac{\mu_B h}{\xi \Delta}$
2.0
1.0
.0
2.0
1.5
1.0
.5
.0
$\left(\frac{k_B T}{\Delta}\right)$
$\frac{J}{\Delta} = 10.0$
2.0
1.0
ξ
1.0
.5
0.

FIG. 1a



$\frac{\mu_B h}{2 < S^z > \Delta}$
2.0
1.0
.0
$\frac{J}{\Delta} = 10.0$
2.0
1.0
$\frac{k_B T}{\Delta}$
.0
.5
1.0
1.5
2.0
$2 < S^z >$
1.0
.5
.0

FIG. 1b

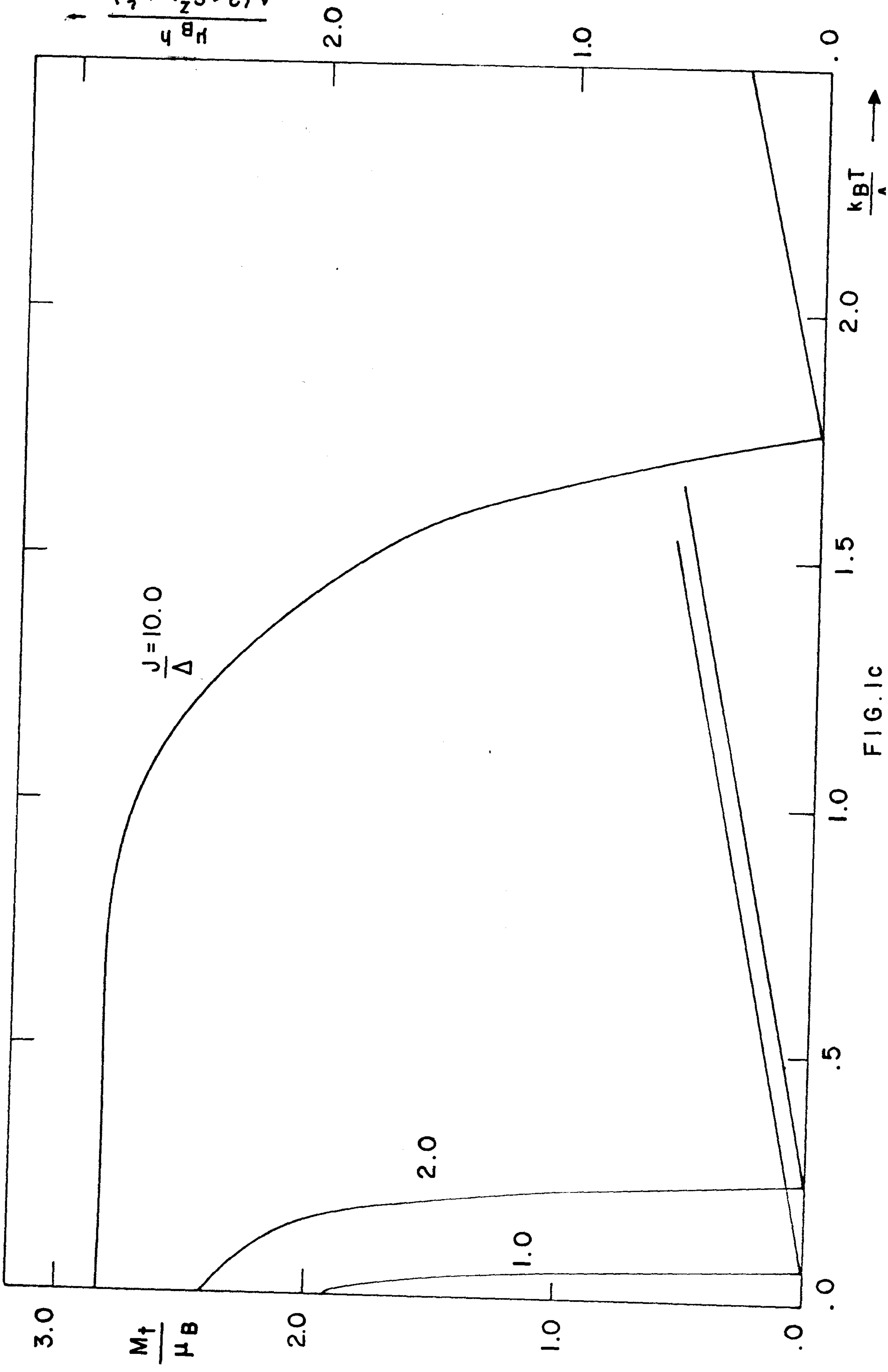


FIG. 1c

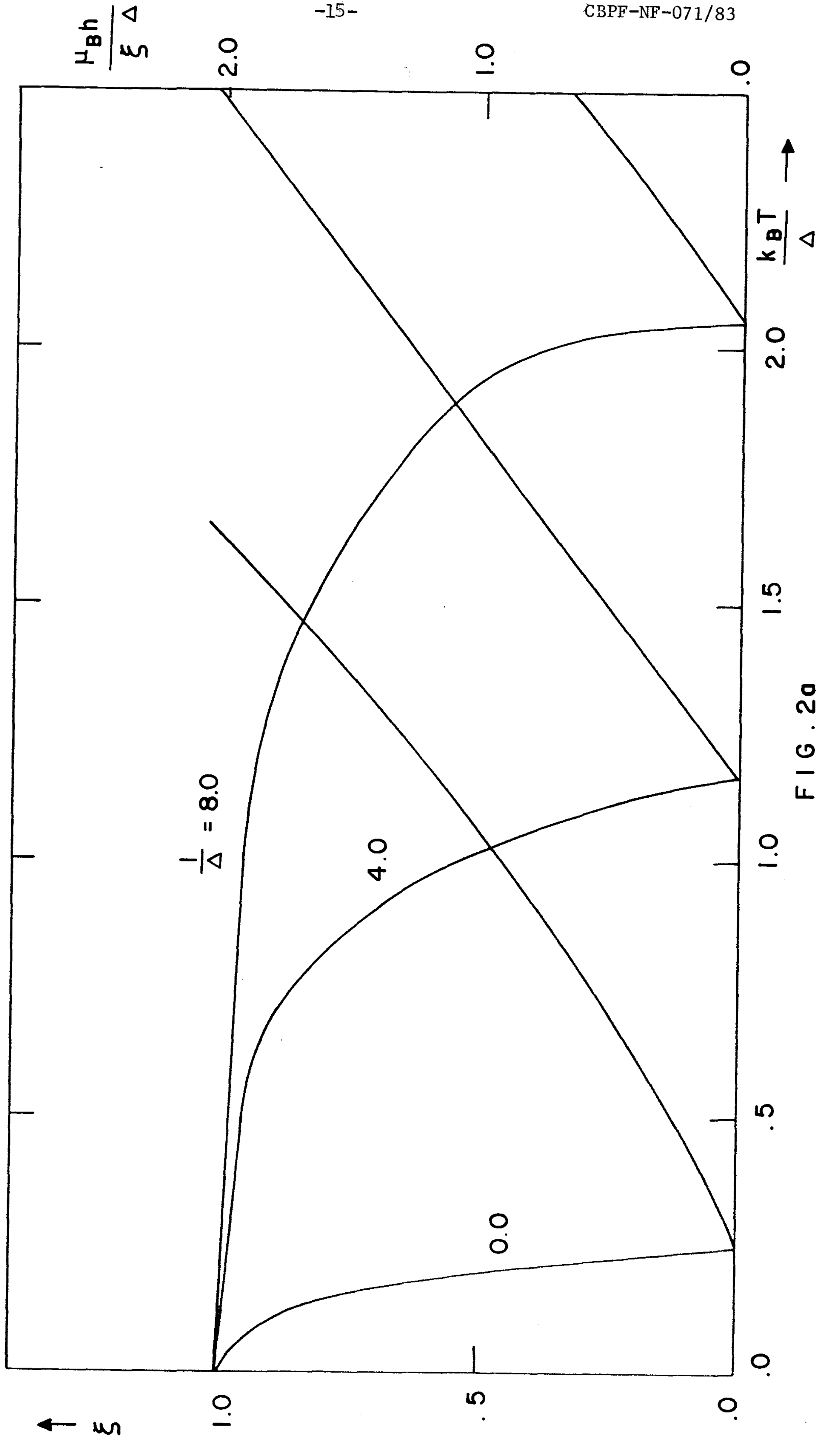

$\frac{\mu_B h}{\xi \Delta}$
2.0
1.0
.0
$\frac{k_B T}{\Delta}$
2.0
1.5
1.0
.5
.0
$\frac{I}{\Delta}$ = 8.0
4.0
0.0
ξ
1.0
.5
.0

FIG. 2a

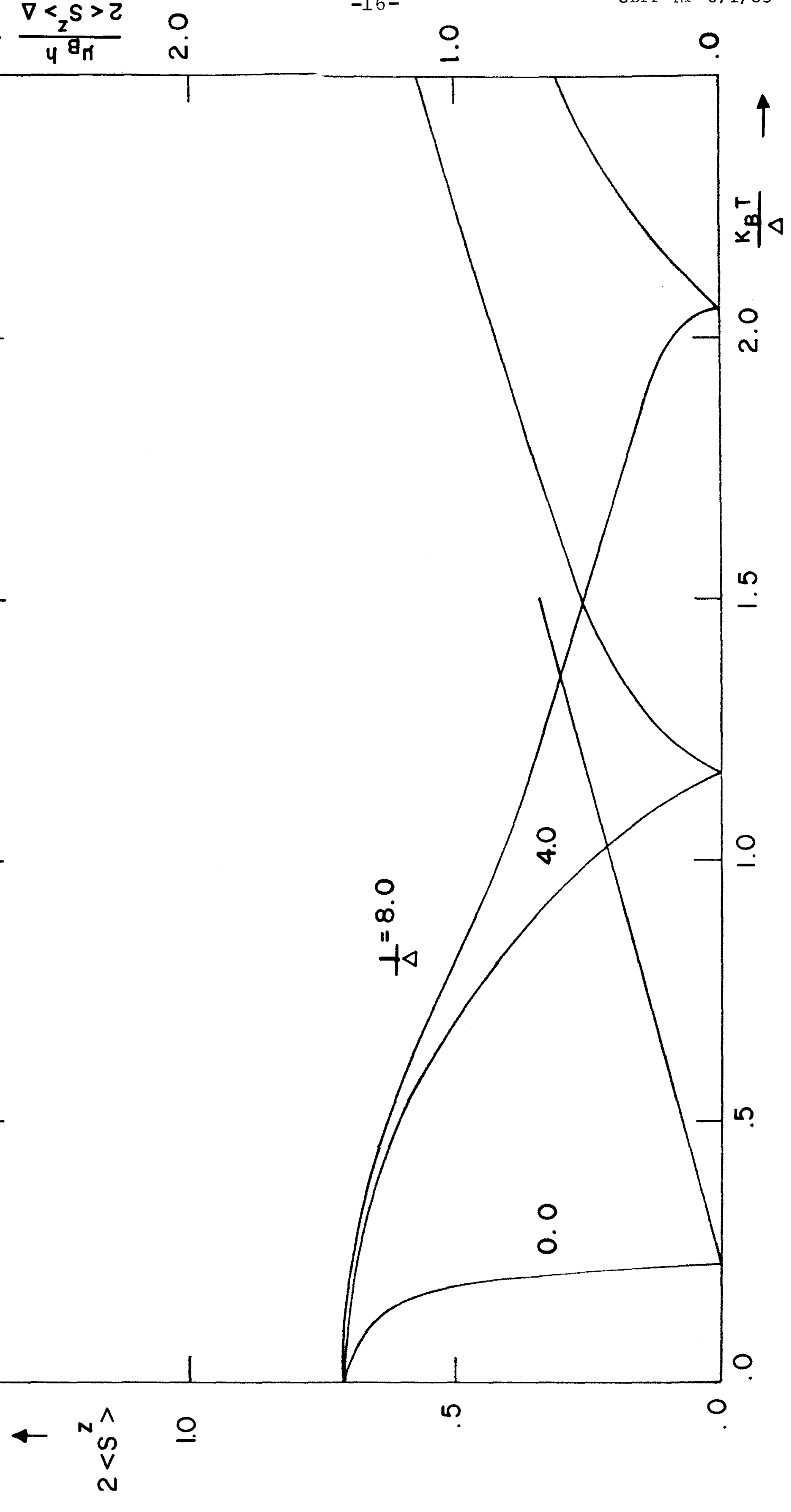


FIG. 2b

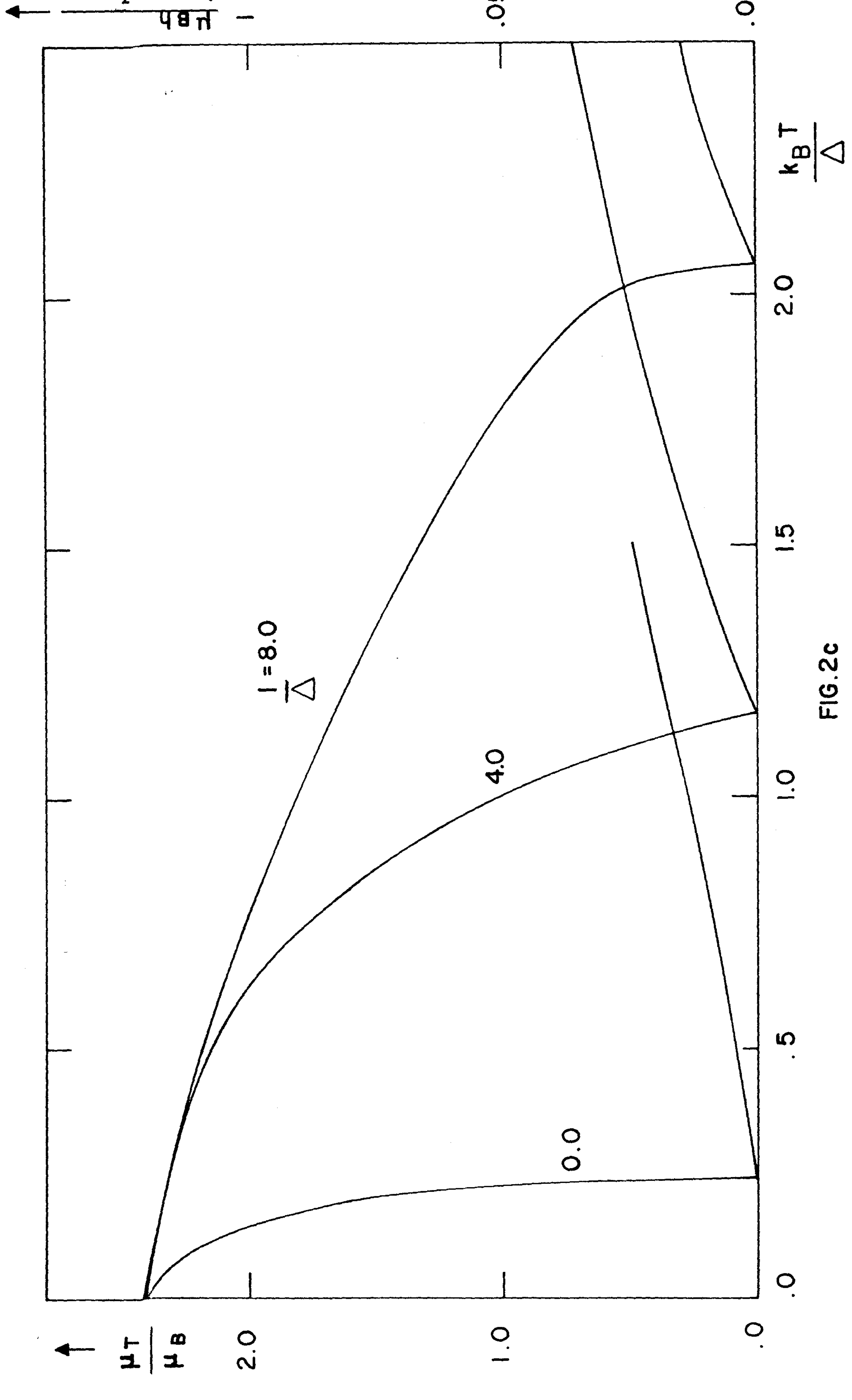


FIG.2c

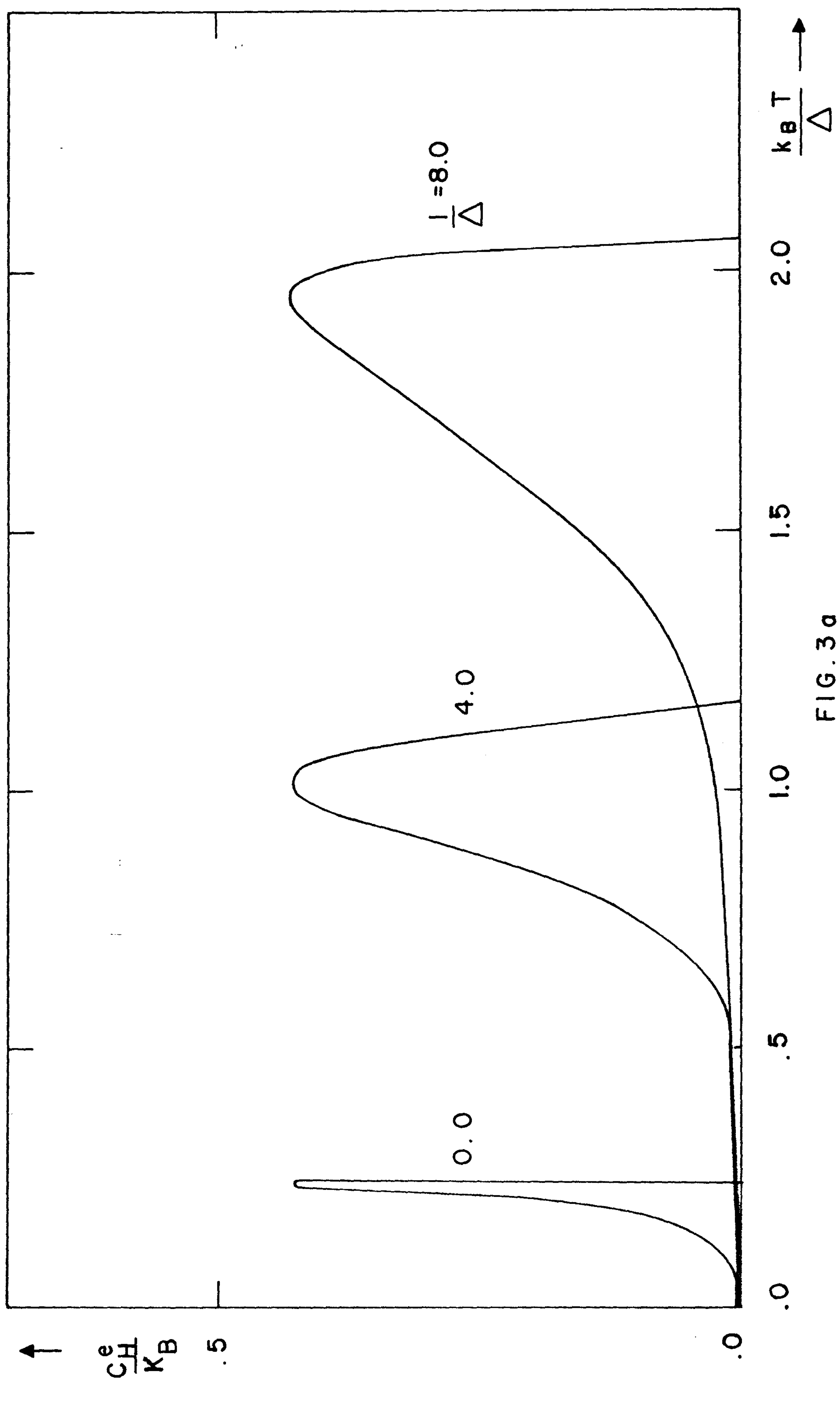


FIG. 3a

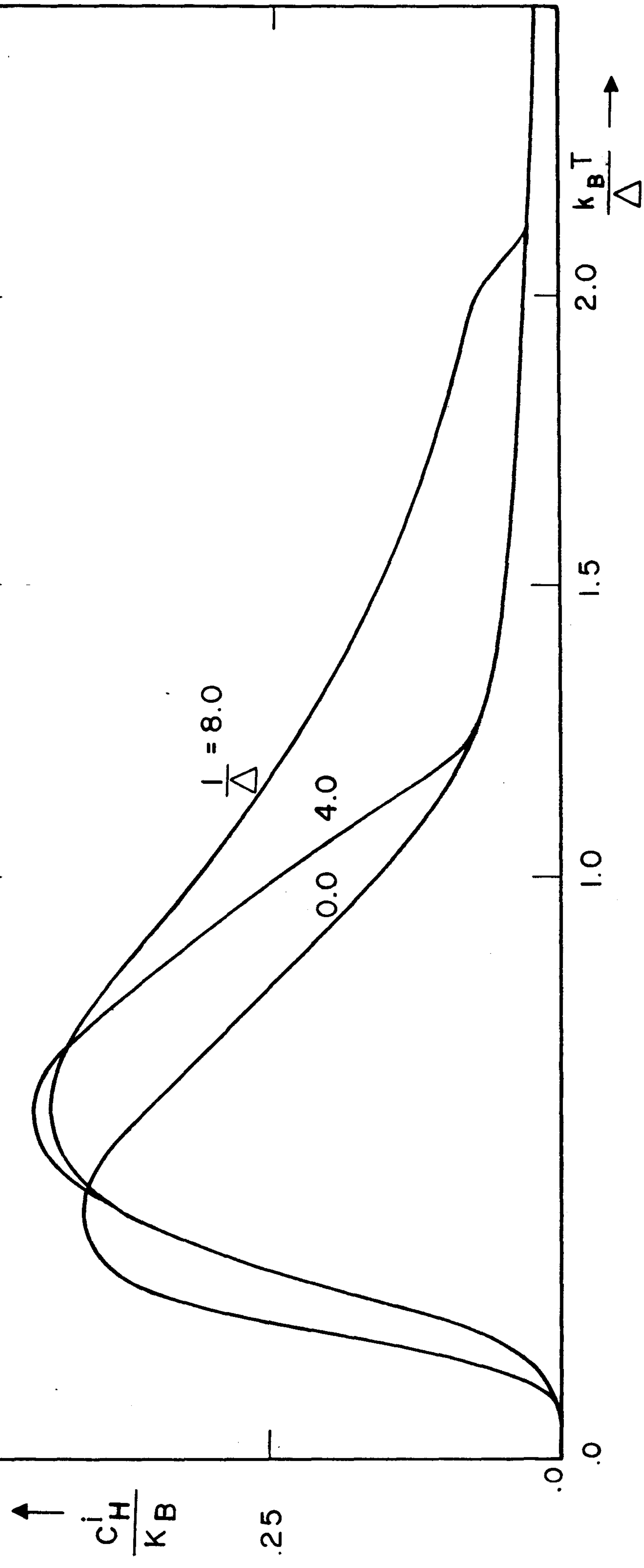


FIG. 3b

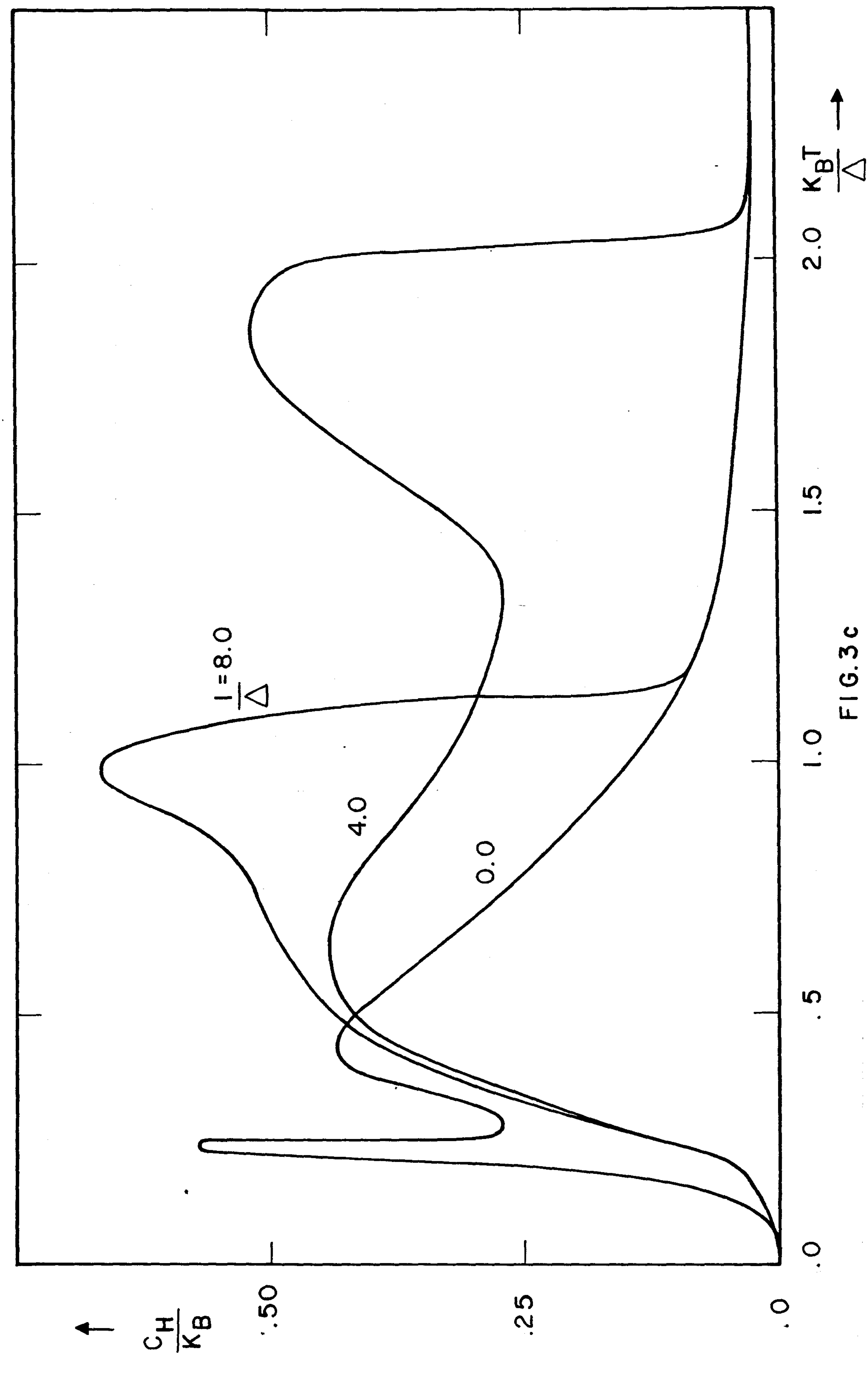


FIG.3c

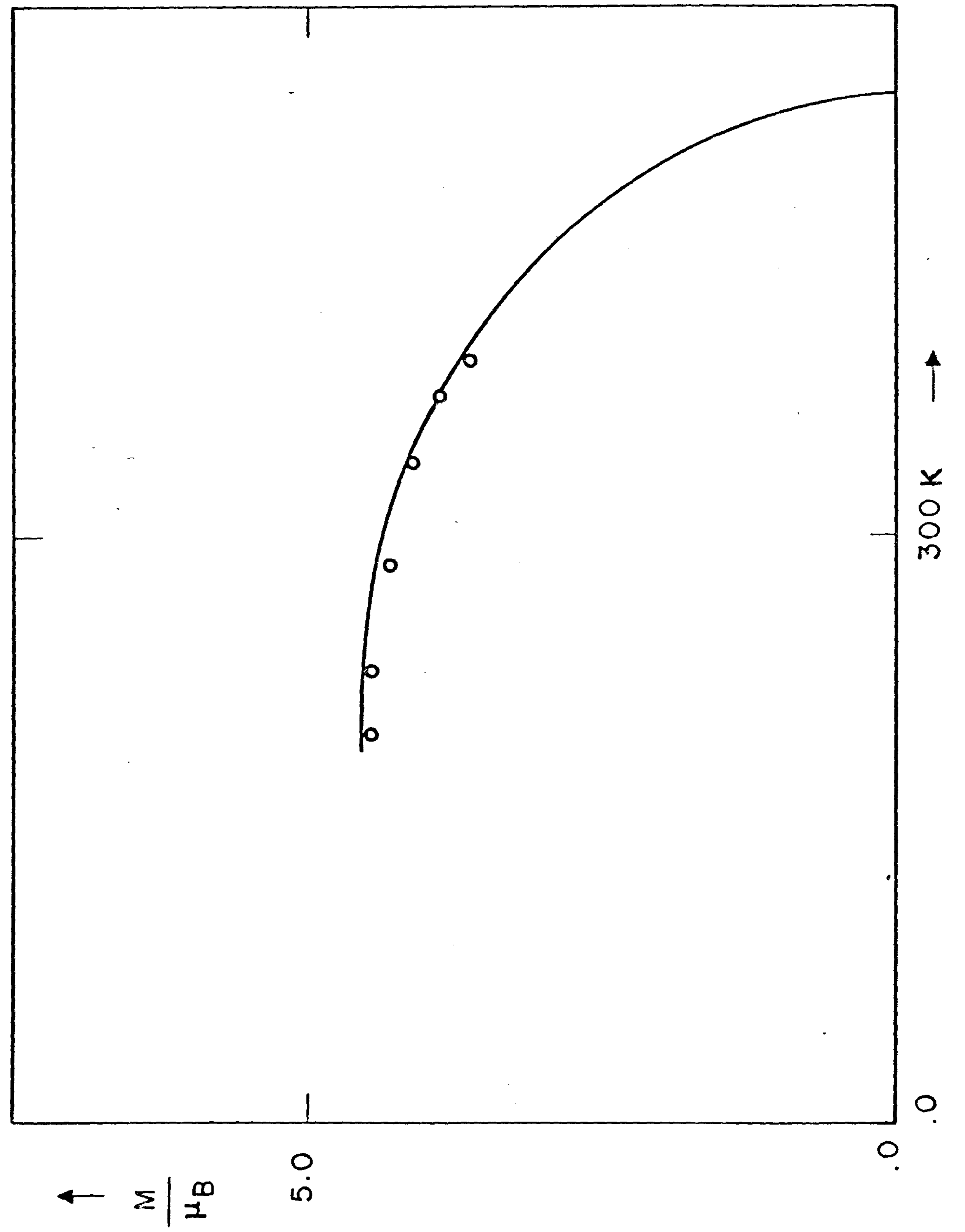


FIG. 4