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THE SPECIFIC HEAT OF SUPERCONDUCTING TRANSITION METALS

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THE SPECIFIC HEAT OF SUPERCONDUCTING  
TRANSITION METALS

C. C. Sung and Lawrence Yun Lung Shen

July 1965

The experimental data on the transition metals of niobium, tantalum and vanadium show marked deviation from the BCS theory for low reduced temperatures<sup>1</sup> ( $t < 0.2$ , here  $t = T/T_c$  and  $T_c$  is the transition temperature).<sup>2</sup> A two-energy-gap model that was proposed by Suhl, Matthias, and Walker<sup>3</sup> is used to obtain an expression for the specific heat of pure and impure superconductors. We are able to fit the data to the expression and determine the following parameters of the two-gap model: the small energy gap  $\Delta_s$ ,  $N_s/N_d$ , ( $N_s, (d)$  is the density of states of s-(d-) band) and the magnitude of inter-band interaction  $J$ .

The Hamiltonian of a pure two-gap superconductor

$$\begin{aligned}
 H = & \sum_{k, \sigma} \epsilon_{ks} S_{k\sigma}^+ S_{k\sigma} + \sum_{k, \sigma} \epsilon_{kd} d_{k\sigma}^+ d_{k\sigma} + J_s \sum_{k, k'} S_{k\uparrow}^+ S_{-k\downarrow}^+ S_{k'\downarrow} S_{-k'\uparrow} \\
 & + J_d \sum_{k, k'} d_{k\uparrow}^+ d_{-k\downarrow}^+ d_{k'\downarrow} d_{-k'\uparrow} + J \sum_{k, k'} (S_{k\uparrow}^+ S_{-k\downarrow}^+ d_{k'\downarrow} d_{-k'\uparrow} + \text{H.C.}) \quad (1)
 \end{aligned}$$

where  $\epsilon_{ks(d)}$  is s-(d-) band kinetic energy measured from the Fermi surface and  $S_{k\sigma}^+ (d_{k\sigma}^+)$   $S_{k\sigma} (d_{k\sigma})$  are the corresponding creation and annihilation operators.  $J_s$ ,  $J_d$ , and  $J$  are the coupling constants of s-s, d-d and s-d bands. In Eq. (1), the summations of  $k$  are extended over values corresponding to the Debye cut off frequency  $\Theta = 0.024$  ev, which is chosen to be the same for both bands. The numerical results of the specific heat are not sensitive to whether different cut off  $\Theta$  are used for different bands.

After the Bogoliubov transformation, the Hamiltonian is reduced to a system of two types of quasi-particles (s-type and d-type) with energies  $E_{k\sigma}^s$  and  $E_{k\sigma}^d$ ;

$$E_k^{s(d)} = [E_{ks(d)}^2 + \Delta_{s(d)}^2]^{1/2} \quad (2)$$

$$f_{ks}^{s(d)} = \frac{1}{e^{E_{ks}^{s(d)}/T} + 1} \quad (3)$$

The equations to determine  $\Delta_s$ ,  $\Delta_d$  and  $T_c$  are:

$$J_d - J \frac{\Delta_d(T)}{\Delta_s(T)} / N_s (J_s J_d - J^2) = \ln \frac{\theta}{\Delta_s(T)} - 2 \sum_{n=0}^{\infty} (-1)^n K_0 \left[ (n+1) \frac{\Delta_s(T)}{T} \right] \quad (4)$$

$$J_s - J \frac{\Delta_s(T)}{\Delta_d(T)} / N_d (J_s J_d - J^2) = \ln \frac{\theta}{\Delta_d(T)} - 2 \sum_{n=0}^{\infty} (-1)^n K_0 \left[ (n+1) \frac{\Delta_d(T)}{T} \right] \quad (5)$$

$$W^2 (J_s J_d - J^2) N_s N_d + (J_s N_s + J_d N_d) W + 1 = 0 \quad (6)$$

where  $W = \ln (0.88 T_c / \theta)$  and  $K_n$  is the modified Bessel function of n-th order. We neglect the interactions between the quasi-particles in our model, and write total entropy as the sum of the entropies of s- and d-quasi-particles. It follows that the electronic specific heat contains two terms:

$$C_{es} = \frac{N_d}{N_s + N_d} C_{es}^d + \frac{N_s}{N_s + N_d} C_{es}^s \quad (7)$$

where

$$C_{es}^d / \gamma T_c = \frac{N_d}{N_s + N_d} \frac{3}{(2\pi)^2} \left( \frac{\Delta_d(T)}{T} \right)^3 \frac{T_c^2}{T} \left\{ \sum_{n=0}^{\infty} (-1)^n (n+1) [K_3(u_d(n)) + 3K_1(u_d(n))] \right. \\ \left. + 4 \frac{d\Delta_d(t)}{d(1/T)} \frac{1}{T\Delta_d(T)} K_1(u_d(n)) \right\} \quad (8)$$

$$u_d(n) = (n+1) \frac{\Delta_d(T)}{T} \text{ and } \gamma = \frac{2}{3} \pi^2 (N_s + N_d) \times (\text{Boltzman Constant})^2$$

By exchanging the label (s) and (d) in Eq. (8) we obtain  $C_{es}^d$ . Which energy gap,  $\Delta_s$  or  $\Delta_d$ , is larger is determined as follows: since

$$N \frac{N_d}{N_s + N_d} \approx 1 \text{ and } \frac{N_s}{N_s + N_d} \ll 1, \quad \Delta_d \text{ has to be assigned as the larger}$$

gap so that at high reduced temperature Eq. (7) gives  $C_{es} \approx C_{es}^d$  which fits the experimental data.<sup>5</sup>  $\frac{N_s}{N_s + N_d} C_{es}^s$  becomes dominant in the low temperature region where

$$T \ll \Delta_d$$

$$\text{Let } x(T) = \frac{\Delta_s(0)}{\Delta_s(T)} \text{ and } \alpha = - \frac{\Delta_d(0)}{\Delta_s(0)} \cdot \frac{J}{(N_s N_d - J^2)}$$

Equation(4) becomes

$$2\sum (-1)^n K_0[(u_s(n))] = \ln x(T) - \alpha(1-x) \quad (8)$$

and

$$\frac{d\Delta_s(T)}{d\left(\frac{1}{T}\right)} \frac{1}{T\Delta_s(T)} = \frac{2u_s(0) \sum_{n=0}^{\infty} (-1)^n (n+1) K_1(u_s(n))}{1 + \alpha x - 2u_s(0) \sum_{n=0}^{\infty} (-1)^n (n+1) K_1(u_s(n))} \quad (9)$$

Parameters used in determining  $C_{es}^s$  are  $N_s/N_d$ ,  $\alpha$ , and  $\Delta_s$ . Eq.(8) is solved numerically for x and substituted in Eq. (9) to obtain  $C_{es}^s$ .  $\Delta_s(0)$  is related to the limiting slope of the electronic specific heat at a low temperature limit. The best fit is given by  $\Delta_s = 0.16T_c$  as shown in Fig. 1. In the temperature region t from 0.14 to 0.1, the peculiar temperature dependence of  $\Delta_s$  accounts for the nearly constant specific heat. See Fig. 3. As shown in Fig. 2,  $\alpha$ , which is related to interband coupling constant J, is an important parameter in this region. Finally, using  $N_s/N_d = 1.5 \times 10^{-2}$  and adding  $C_{es}^s$  to  $C_{es}^d$  we obtain the solid curve shown in Fig. 2.

We note that the parameter to measure the strength of interband coupling

$$\frac{J(N_s N_d)^{1/2}}{J_s N_s J_d N_d} = \alpha \left( \frac{N_s}{N_d} \right)^{1/2} \approx 0.06.$$

From the parameters  $\Delta_s$ ,  $\Delta_d$  and  $N_s/N_d$ , which are determined by fitting the data and Eqs. (4,6), we can calculate  $J_d$ ,  $J_s$  and  $J$ . However, because of the small values of  $N_s/N_d$  and  $\Delta_s/\Delta_d$  and the large experimental uncertainty of  $T_c$  and  $\Delta_d$  we are unable to obtain reliable values of  $J_d$ ,  $J_s$  and  $J$ .

The above model gives a reasonable specific heat of pure niobium over the whole measured temperature range. Even though detailed band structure calculations are lacking in niobium, we get  $N_s/N_d$  from specific heat alone. The discrepancy between experimental value and calculation may be due to (1) the pure sample is not 100% pure as it is assumed in the calculation and (2) the simplification of the used model. No effort was made to fit tantalum data because they are not available over a wide enough reduced temperature range.

In our calculation of the effect of impurities on the specific heat, we take the impurities to be non-magnetic. The only effect of the impurities taken into account is the transition between s-quasi-particle and d-quasi-particle states.

The effective Hamiltonian is

$$H_{\text{eff}} = \sum_{k\sigma} E_{k\sigma}^d \gamma_{k\sigma}^{d+} \gamma_{k\sigma}^d + \sum_{k\sigma} E_{k\sigma}^s \gamma_{k\sigma}^{s+} \gamma_{k\sigma}^s + J' \sum_{k;\sigma} (\gamma_{k\sigma}^{d+} \gamma_{k\sigma}^s + \text{H. C.}) \quad (10)$$

here  $\gamma_{k\sigma}^{d+}$  ( $\gamma_{k\sigma}^{s+}$ ) is the creation operator of d-(s-) quasi particles and  $J'$  is proportional to the density of impurities.



In Eq. (10), the scattering of the s- and d- quasi-particles with the impurities into the same energy band is neglected, since this effect of the scattering is to smear the Fermi surface in each band and is presumably small. We can ignore the difficult problem of finding the eigenstates<sup>6</sup> of the quasi-particles in the presence of impurities, because of the small amount of impurities which cause no observable effect for  $T_c > 0.2$ .<sup>5</sup>

$H_{\text{eff}}$  is easily diagonalized with the new quasi-particles energies  $E_{k\sigma}^1$  and  $E_{k\sigma}^2$ . Here

$$E_{k\sigma}^1 = \cos^2 \theta_k E_{k\sigma}^d + \sin^2 \theta_k E_{k\sigma}^s$$

$$E_{k\sigma}^2 = \sin^2 \theta_k E_{k\sigma}^s + \cos^2 \theta_k E_{k\sigma}^d$$

and

$$\tan 2\theta_k = \frac{J'}{E_{k\sigma}^d - E_{k\sigma}^s}$$

Because  $E_{k\sigma}^s/E_{k\sigma}^d \ll 1$ ,  $E_{k\sigma}^1 \approx E_{k\sigma}^d$ .  $E_{k\sigma}^2$  is approximately equal to

$$E_{k\sigma}^s + \frac{1}{4} \frac{J'^2}{E_{k\sigma}^d - E_{k\sigma}^s} \approx E_{k\sigma}^s + \frac{1}{4} \frac{J'^2}{\Delta_d} \quad (11)$$

in the region where  $\epsilon_{ks} < \Delta_d$ . In computing C the contribution of this region dominates, and Eq. (11) is a good approximation.

$$C_{es}^{\text{impure}} = \frac{N_d}{N_s + N_d} C_{es}^d + \frac{N_s}{N_s + N_d} C_{es}^s \quad (12)$$

here

$$C_{es}^s / \gamma T_c = \frac{N_s}{N_s + N_d} \frac{3}{(2\pi)^2} \left( \frac{\Delta_s(T)}{T} \right)^3 \frac{T_c^2}{T^2} \left\{ \sum_n (-1)^n e^{-(n+1)C/T} \right.$$

$$[(n+1) \cdot K_3(u_s(n)) + 3K_1(u_s(n)) + g + 4 \frac{d\Delta_s(T)}{d(\frac{1}{T})} \frac{1}{T\Delta_s(T)} f ]]$$

$$g = [(n+1) \frac{C^2}{\Delta_s^2} \frac{2C}{\Delta_s u} ] K_1(u_s(n)),$$

$$f = (n+1) K_1(u_s(n))$$

$$C = \frac{J'^2}{\Delta_d}$$

It is impossible to use Eq. (12) to fit the experimental data without introducing an additional parameter, Z, which is multiplied to the  $C_{es}$  of Eq. (12) to obtain the curves in Fig. 1. Since Z is much less than one, the simple calculation shows that the electronic structure of impurities<sup>7</sup> in transition metals has to be taken into account to explain the experimental data.

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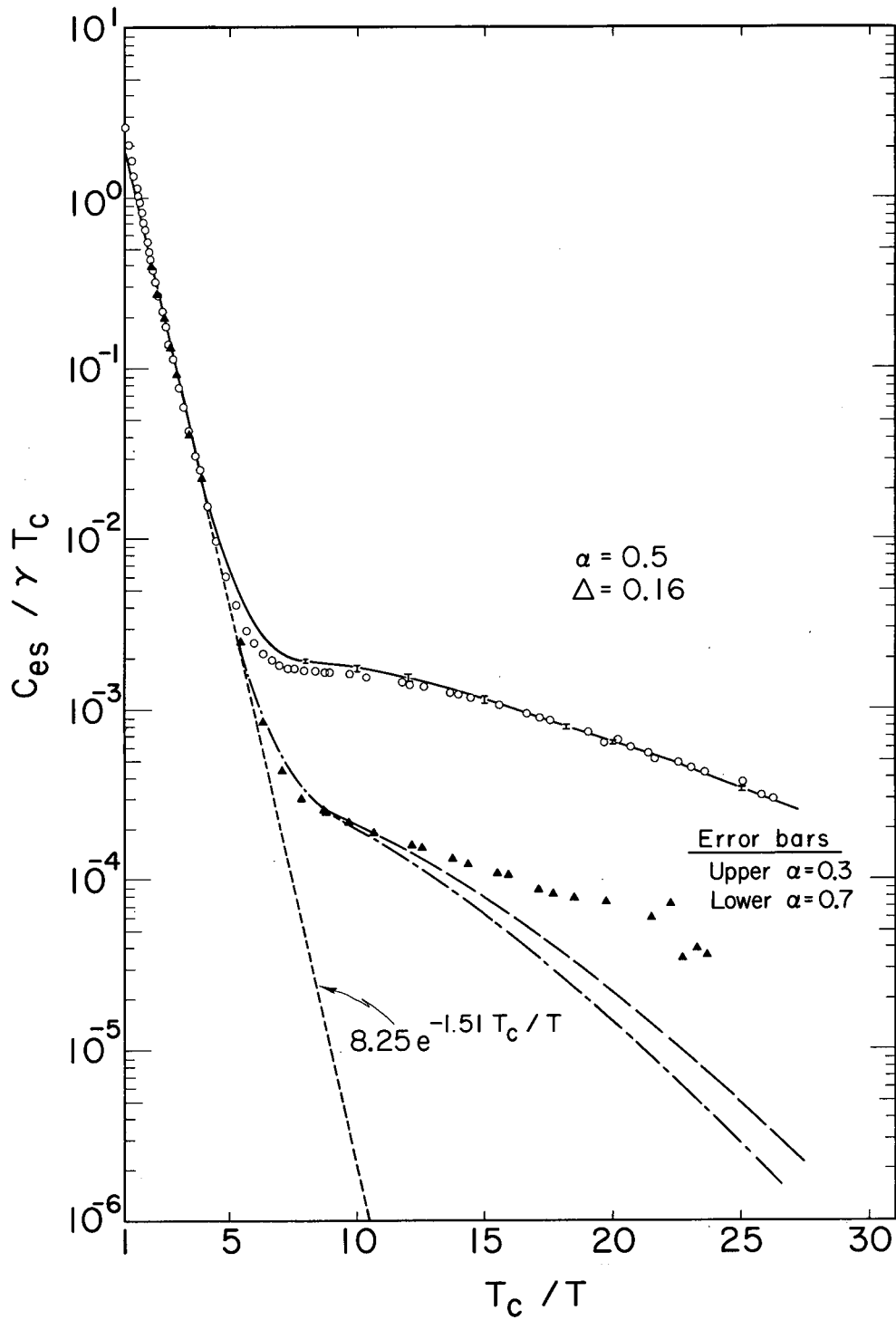
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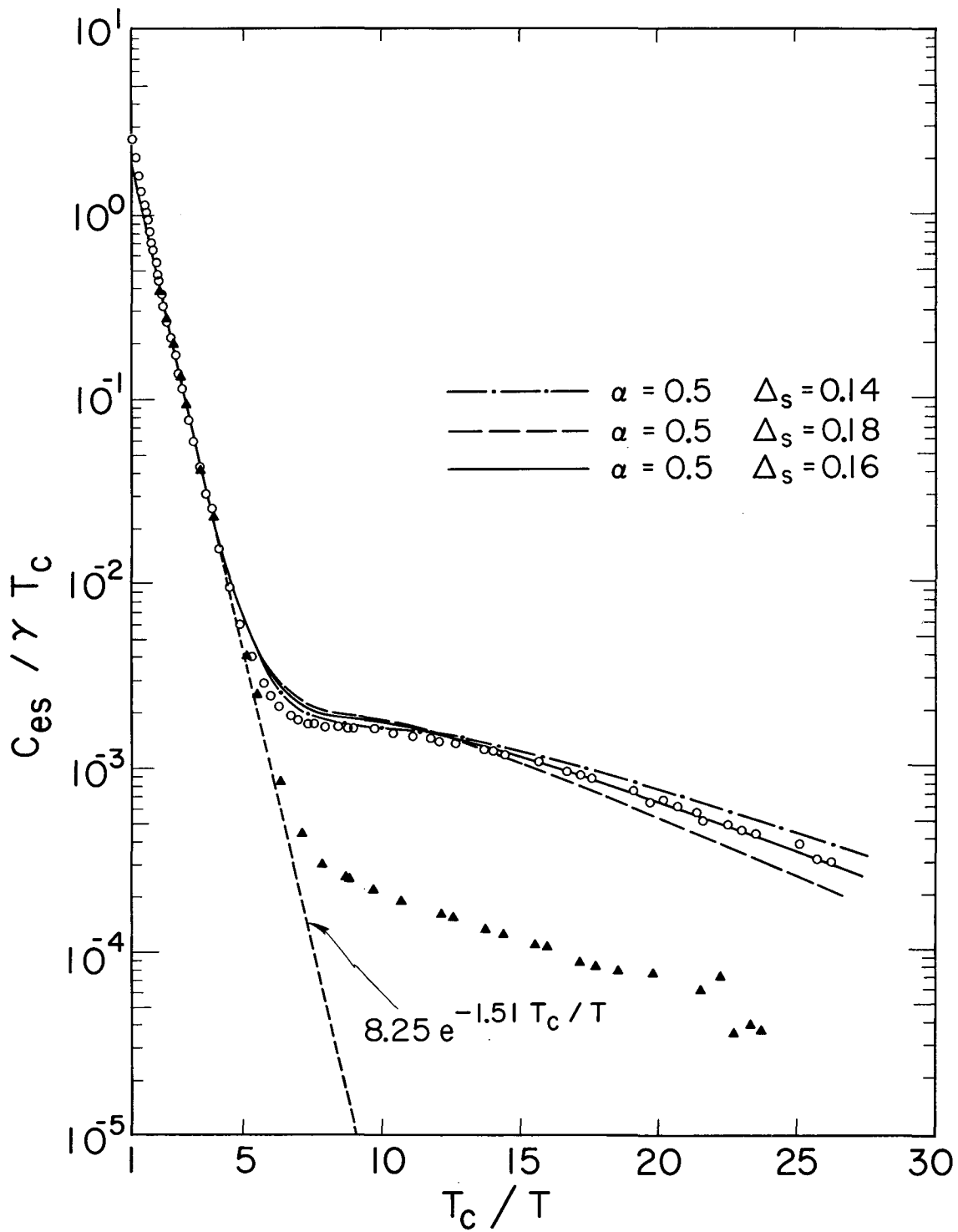
Figure Captions

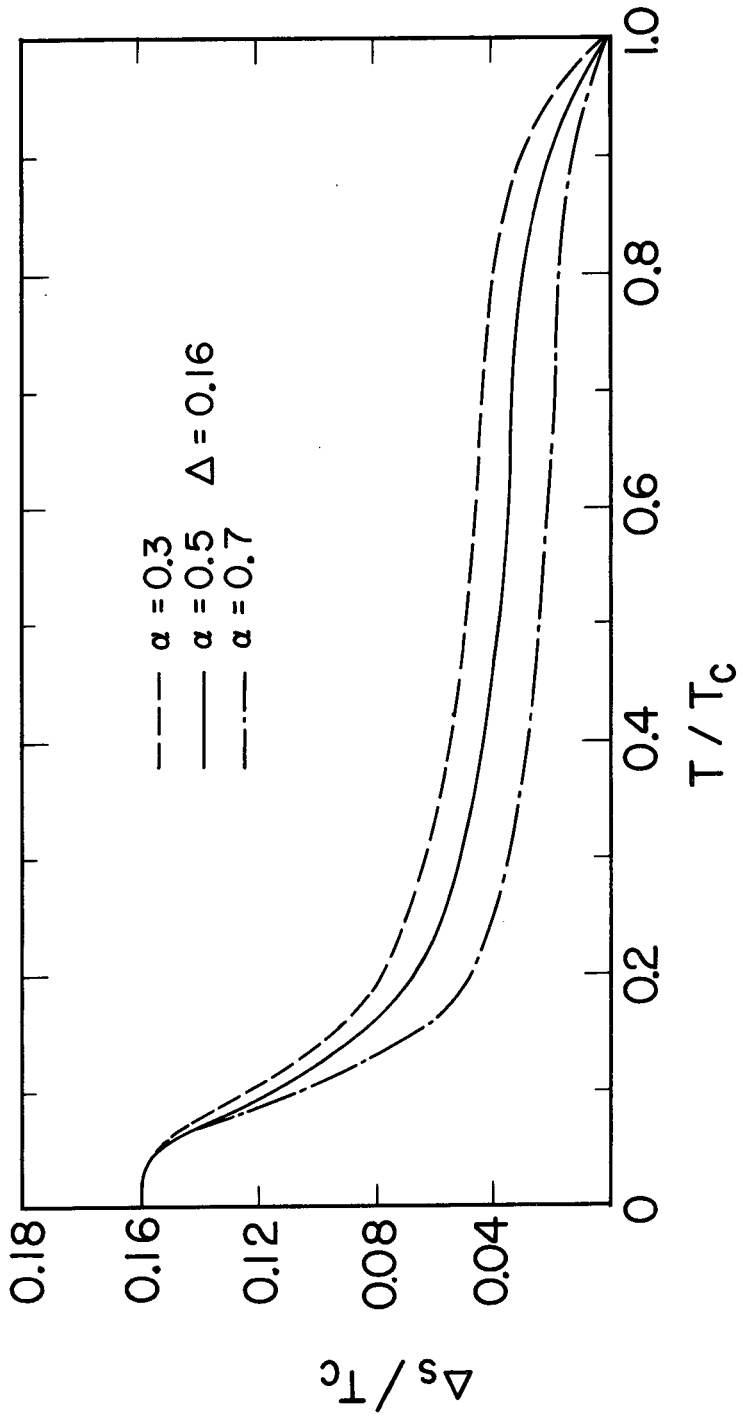
Fig. 1 The calculated  $C_{es}$  for different  $\alpha$ 's. The points denote the experimental data. The upper dashed curve and the lower dashed curve are obtained from Eq. (12) with  $C = \frac{T_e}{6}$  and  $\frac{T_c}{8}$ .  $Z = 0.30$  and  $0.43$ , respectively.

Fig. 2 The calculated  $C_{es}$  for various value of  $\Delta_s(0)$ .

Fig. 3 The second energy gap  $\Delta_s(T)$  for various  $\alpha$ .







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