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16. Summary/Notes

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EXTRINSIC SPECIFIC HEAT OF PHOSPHORUS DOPED SILICON

M. Fabbri, I.C. da Cunha Lima and A. Ferreira da Silva

Instituto de Pesquisas Espaciais - INPE

Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq

12200 S.J. dos Campos, SP, Brazil

ABSTRACT

The theory of Matsubara and Toyozawa developed for impurity bands in semiconductors is investigated further in order to calculate the specific heat of Si:P. The effect of correlation as well as overlap on the electron hopping energy integral is taken into account via Heitler-London two-particle wave functions. The calculated specific heat shows good agreement when compared to the experimental data over a wide range of impurity concentration around the critical value for MNM transition. The comparison between MT and AMO-MT calculations shows a big enhancement due to electron correlation. The results of the highly-correlated-electron-gas model and inhomogeneity model are shown for the sake of comparison.

The correlation effect as well as disorder in doped semiconductors have given rise to considerable interest in a large number of experimental and theoretical studies. The experimental results of electric conduction (Fritzsche 1958, Yamanouchi et al. 1967, Toyotomi and Morigaki 1968) and of specific heat (Marko et al. 1974, Kobayashi et al. 1977, Sasaki 1979) as well as the theoretical investigations (Ishida and Yonezawa 1973, Aoki and Kamimura 1976) suggest that the Mott-Hubbard-Anderson (MHA) scheme, in which electron correlation and Anderson localization play the most essential roles, provides a proper description of the novel behavior of doped semiconductors near the metal-non-metal (MNM) transition. Matsubara and Toyozawa (1961) who will henceforth be referred to as MT, carried out one of the earliest theoretical studies along the lines of the MHA scheme. They developed a one-band model which treats the random distribution of the impurities by the Green's function technique, but have neglected the correlation between both electrons and impurities. Their scheme have recently been improved (Chao and Ferreira da Silva 1978a, Osorio et al. 1978) by incorporating the alternant-molecular-orbital (AMO) method (Pauncz 1967), to the MT theory. This AMO-MT scheme, yields and enhanced density of states of the impurity band and yields a specific heat in reasonable agreement with the measured values (Chao and Ferreira da Silva 1979a) around the critical impurity concentration for the MNM transition.

Since in our case the narrowing of the impurity band has its origin in the reduction of electron hopping integrals V_{ij}, we introduce the correlation effect into these matrix elements. Therefore,

instead of using a single-particle wave function, we use a Heitler-London (HL) two-particle wave function, as was proposed by Chao et al. (1977), to obtain V_{ij}. The calculated specific heat for phosphorus doped silicon (Si:P) is in good agreement with the experimental data. For comparison we show the results of the highly-correlated-electron-gas model and the inhomogeneity model.

An isolated impurity in a host semiconductor of static dielectric constant K_h can be considered as an ion core plus one weakly bound electron. The ground state wave function is a hydrogen-like 1s function

$$\phi(\vec{r}) = (1/\pi a_H^{*3})^{1/2} \exp(-r/a_H^*) \tag{1}$$

The effective Bohr radius a_H^* is usually determined from the experimental ionization energy ε_I (Edwards and Sienko 1978), via $e^2/2K_h\varepsilon_I$.

In view of the hydrogenic type impurity orbital for an isolated impurity, an accurate calculation can be done using a Heitler-London two-particle wave function

$$\Psi(ij;\vec{r}_1\vec{r}_2) = \beta\,[\phi(\vec{r}_1-\vec{R}_i)\phi(\vec{r}_2-\vec{R}_j)+\phi(\vec{r}_1-\vec{R}_j)\phi(\vec{r}_2-\vec{R}_i)] \tag{2}$$

where β is the normalization constant. Therefore, we consider a pair of neutral impurities located at $\vec{R}_i$ and $\vec{R}_j$, with $\vec{r}_1$ and $\vec{r}_2$ labelling the coordinates of the two electrons, forming an H_2-like impurity molecule. The Hamiltonian is written as

$$H = -\frac{1}{2}\sum_p \nabla_p^2 - \sum_{p,q} |\vec{r}_p-\vec{R}_q|^{-1} + \frac{1}{r_{12}} + \frac{1}{R_{ij}} \tag{3}$$

where

$p = 1,2$ $\qquad$ $r_{12} = |\vec{r}_1-\vec{r}_2|$

$q = i,j$ $\qquad$ $R_{ij} = |\vec{R}_i-\vec{R}_j|$

We choose units such that $m = \hbar = e^2/K_h = 1$. The lowest energy state of the impurity molecule

$$E = \langle \Psi (ij;\vec{r}_1\vec{r}_2) \mid H \mid \Psi (ij;\vec{r}_1\vec{r}_2) \rangle \tag{4}$$

can be calculated analytically in terms of the Slater (1968) integrals S, K, J, J' and K':

$$E (\alpha,R_{ij}) = \frac{1}{2 (1+S^2)} \left[2\alpha^2(1-KS-S^2) + \alpha(J'+K'+4KS+2J-4) + \frac{1}{R_{ij}} \right] \tag{5}$$

and α $(1/a_H)$ can be treated as a variational parameter. The normalization constant of the lowest-energy state is $\beta = |2(1+S^2)|^{-1/2}$ where $S = \langle\phi(\vec{r}-\vec{R}_i) \mid \phi(\vec{r}-\vec{R}_j)\rangle$ is the overlap integral. The ground state energy and the equilibrium separation of the impurity molecule are found by a minimization of the energy $\partial E(\alpha,\mathbf{R}_{ij})/\partial\alpha=0$. We found satisfactory agreement with the other calculations and experimental results. At the equilibrium distance (R=1.43 a.u.) the energy is quoted as -2.278 Ry. For large separation $(R \to \infty)$ the problem reduces to $\alpha = 1$ (isolated hydrogen atoms), and for $R = 0$ it corresponds to a helium atom, $\alpha = 1.6875$.

The original scheme for doped semiconductors starts from a tight binding hamiltonian

$$H = \sum_i E_i a_i^\dagger a_i + \sum_{i\neq j} V(\vec{R}_{ij})a_i^\dagger a_j = E_d \sum_i a_i^\dagger a_i + \sum_{i\neq j} V(\vec{R}_{ij})a_i^\dagger a_j \tag{6}$$

for a single impurity band, where $a_i^\dagger$ and a_i are the creation and the annihilation operators respectively of an electron at the ith impurity site. The one-site energy can be assumed to be constant (Chao and Ferreira da Silva 1978b). As measured from the host conduction band, it can be taken as $E_d = -\varepsilon_I$, the ionization energy of an isolated

impurity. Here we take this as our energy origin. The $V(\vec{R}_{ij})(\equiv V_{ij})$ is the energy integral for the transfer of an electron from the ith site to the jth site:

$$V_{ij} = \int \phi(\vec{r}-\vec{R}_i)H(\vec{r})\phi(\vec{r}-\vec{R}_j)d\vec{r} = - V_0(1+\alpha R_{ij}) \exp(-\alpha R_{ij}) \tag{7}$$

where $H(r) = \dfrac{-e^2}{K_h \, |\vec{r}-\vec{R}_i|}$

and V_0 is equal to twice the ionization energy, $V_0=2|E_d|$. Since we are going to deal with a two-particle Hamiltonian, and in order to keep the MT scheme intact, we have to single out the hopping of only the first electron in the combined field of the impurity ions and the second electron. Consequently, we will introduce an effective one-electron Hamiltonian $\tilde{H}(r)$ as

$$[\phi(\vec{r}_1-\vec{R}_i) + \phi(\vec{r}_1-\vec{R}_j)|\tilde{H}(\vec{r}_1)|\phi(\vec{r}_1-\vec{R}_i)+\phi(\vec{r}_1-\vec{R}_j)]$$

$$= \int \Psi(ij;\vec{r}_1\vec{r}_2)\ (H - \frac{1}{R_{ij}})\ \Psi(ij;\vec{r}_1\vec{r}_2)d\vec{r}_2 \tag{8}$$

The effective one-electron matrix elements can be written as

$$V_{ij} = \int \phi(\vec{r}-\vec{R}_i)\tilde{H}(\vec{r})\,\phi(\vec{r}-\vec{R}_j)d\vec{r} \tag{9}$$

From this relation we can find for i=j the diagonal matrix elements

$$V_{ii} = \frac{1}{2(1+S^2)}\left[\alpha^2 + \alpha\left(J + \frac{J'}{2} - 2\right)\right] \tag{10}$$

and for $i \neq j$ the off-diagonal matrix elements

$$V_{ij} = \frac{1}{2(1+S^2)}\left[\alpha^2\ (KS+S^2) + \alpha\left(2KS + \frac{K'}{2}\right)\right] \tag{11}$$

The optimum values obtained for α when we minimise the ground state energy are introduced in V_{ii}, as well as in V_{ij}.

The Green's functions defined by

$$G_{mn}^{(\pm)}(E) = \langle 0 | a_m \frac{1}{E-H\pm i\varepsilon} a_n^{\dagger} | 0 \rangle \tag{12}$$

$$G_{mn}(E) = \frac{i}{2\pi} \left[G_{mn}^{(+)}(E) - G_{mn}^{(-)}(E) \right] \tag{13}$$

enable us to calculate the density of states. They are calculated from (6) with configuration averaging over the random distribution of impurities. For the sake of simplicity, we only give the results of the MT scheme. For detailed calculation, the reader should refer to the MT original work. Defining

$$\xi^{(\pm)} = Z_{\pm} < G_{mn}^{(\pm)}(E) > \tag{14}$$

where $<\cdots>$ means configuration averaging and $Z_{\pm} = E\pm i\varepsilon$, then $\xi^{(\pm)}$ satisfies the equation

$$1 - 1/\xi^{(\pm)} = \frac{N\,\xi^{(\pm)}}{8\pi^3 Z_{\pm}^2} \int \frac{\nu(\vec{k})d\vec{k}}{1-(N\xi^{\pm}/Z_{\pm})\nu(\vec{k})} \tag{15}$$

where $\nu(\vec{k})$ is the Fourier transform of V_{ij}.

The density of states is then

$$D(E) = \frac{i}{2\pi} \frac{N(\xi^{+}-\xi^{-})}{E} = -\frac{N}{\pi} \operatorname{Im}\left(\frac{\xi^{+}}{E}\right) \tag{16}$$

where N is the impurity concentration.

The impurity density of states as well as the Fermi energy were calculated and were plotted for various values of the normalized impurity concentrations $P = 32\pi N a_H^{*3}$ in Figure 1, and are compared with MT. We notice how the electron correlation substantially reduces the impurity bandwidth. If we look at the off-diagonal matrix elements V_{ij} as a function of the interimpurity distance, we see that it has a

form similar to that obtained by MT and AMO-MT (Chao and Ferreira da Silva 1978b). However, the magnitude of V_{ij} (HL) is reduced, specially, for large R_{ij}, i.e., $|V_{ij}\,(HL)|<|V_{ij}\,(AMO)|<|V_{ij}\,(MT)|$. Then the long range hopping of electrons is effectivelly cut off by the electron correlation. The Fermi energy E_F is determined by numerical integration from

$$2\int_{-\infty}^{E_F} D(E)\,dE=N \tag{17}$$

Knowing the density of states for various impurity concentrations one can obtain the specific heat. First we calculate the total energy of the impurity electrons,

$$\bar{E}(T) = \int ED(E)f(E,T)dE \tag{18}$$

where f(E,T) is the Fermi distribution function. The specific heat is then

$$C(T) = \frac{d\bar{E}}{dT} = \int ED(E)\,\frac{df(E,T)}{dT}\,dE \tag{19}$$

It is worth-while to point out that keeping only the lower order terms in the Sommerfeld expansion, the low temperature specific heat can be well approximated by

$$C(T) = \frac{\pi^2 k_B^2}{3}\,D(E_F)T = \gamma T \tag{20}$$

where k_B is the Boltzmann constant.

Calculating γ from (2D) and C(T)/T from (19) numerically, a discrepancy of less than 1% is found in a wide range of impurity concentration for $T < 5^{\circ}K$. The electronic specific heat coefficient γ for Si:P as

function of the impurity concentration, representing HL-MT, is plotted in Figure 2 as curve 1. We see that the strong electron correlation effect shows a larger enhancement than AMO-MT, curve 2 and the MT calculations, curve 3. For comparison's sake, we also plot γ, curve 4, calculated with a highly-correlated-electron-gas model by Berggren (197B) and Sernelius (197B).Their model is valid in the metallic region $N>N_C$, where it gives good agreement with experiment. The dots with error bars are the experimental data (Kobayashi et al. 1977, Sasaki 1979). The experimental critical impurity concentration $N_C = 3.2 \times 10^{18}$ cm^{-3} or $P_C = 0.74$ is indicated with an arrow. The Bohr radius obtained from the experimental ionization energy (Edwards and Sienko 1978) is 13.2Å.

In Figure 3, we show the specific heat for Si:P obtained from (19) by numerical integration,as a full line. The dotted line refers to the inhomogeneity model and solid circles correspond to the experimental data, both carried out by Marko et al. (1974). In conclusion we have shown how sensitive the specific heat is, in phosphorus doped silicon to changes in electron correlation, presenting a satisfactory agreement between our calculation and experiment over a wide range of impurity concentration.

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FIGURE CAPTIONS

Fig. 1. Density of states of impurity bands for various values of impurity concentrations P. Full line corresponds to our calculation. Dot-das hed lines refer to the MT calculation. The position of the Fermi energy is indicated by dashed lines and the bottom of the host conduction band by dotted line.

Fig. 2 . Electronic specific heat coefficient γ for Si:P as function of the impurity concentration N. Curve 1 is the present calculation. Curve 2 is the AMO-MT calculation. Curve 3 is the MT calculation. Curve 4 is the result from the highly correlated-electron-gas model. The dots with error bars are the experimental data measured by W. Sasaki and co-workers. N_c indicates the impurity critical concentration for MNM transition.

Fig. 3. The electronic specific heat of Si:P in units of J/ok-mole as function of temperature for impurity concentration 5.9×10^{18} cm^{-3}. Full line corresponds to the present calculation. Dotted lines refer to the inhomogeneity model by Marko et al. (1974). Solid circles correspon to the experimental data by Marko et al (1974)

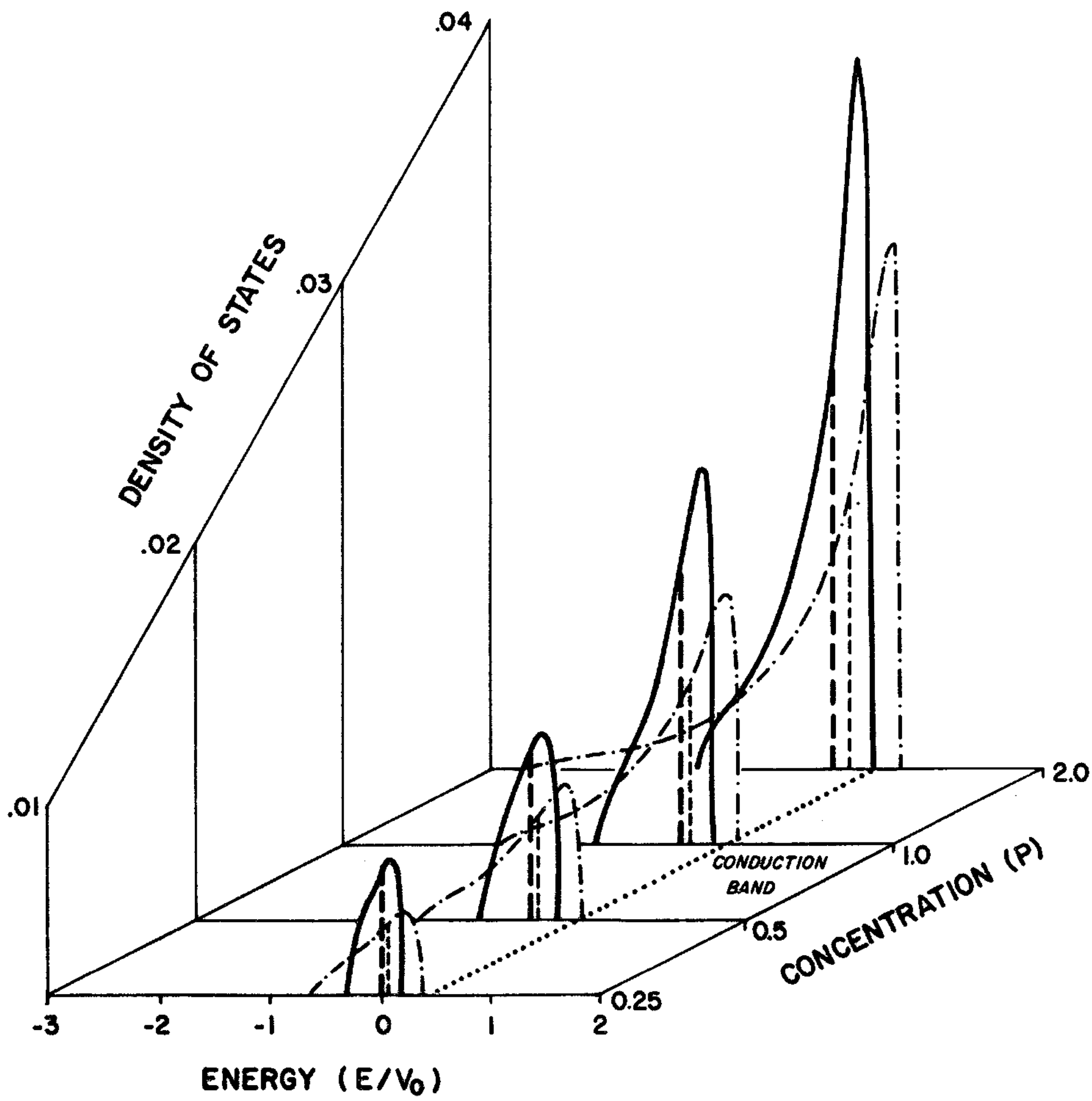

Fig. 1 M. Fabbri et al

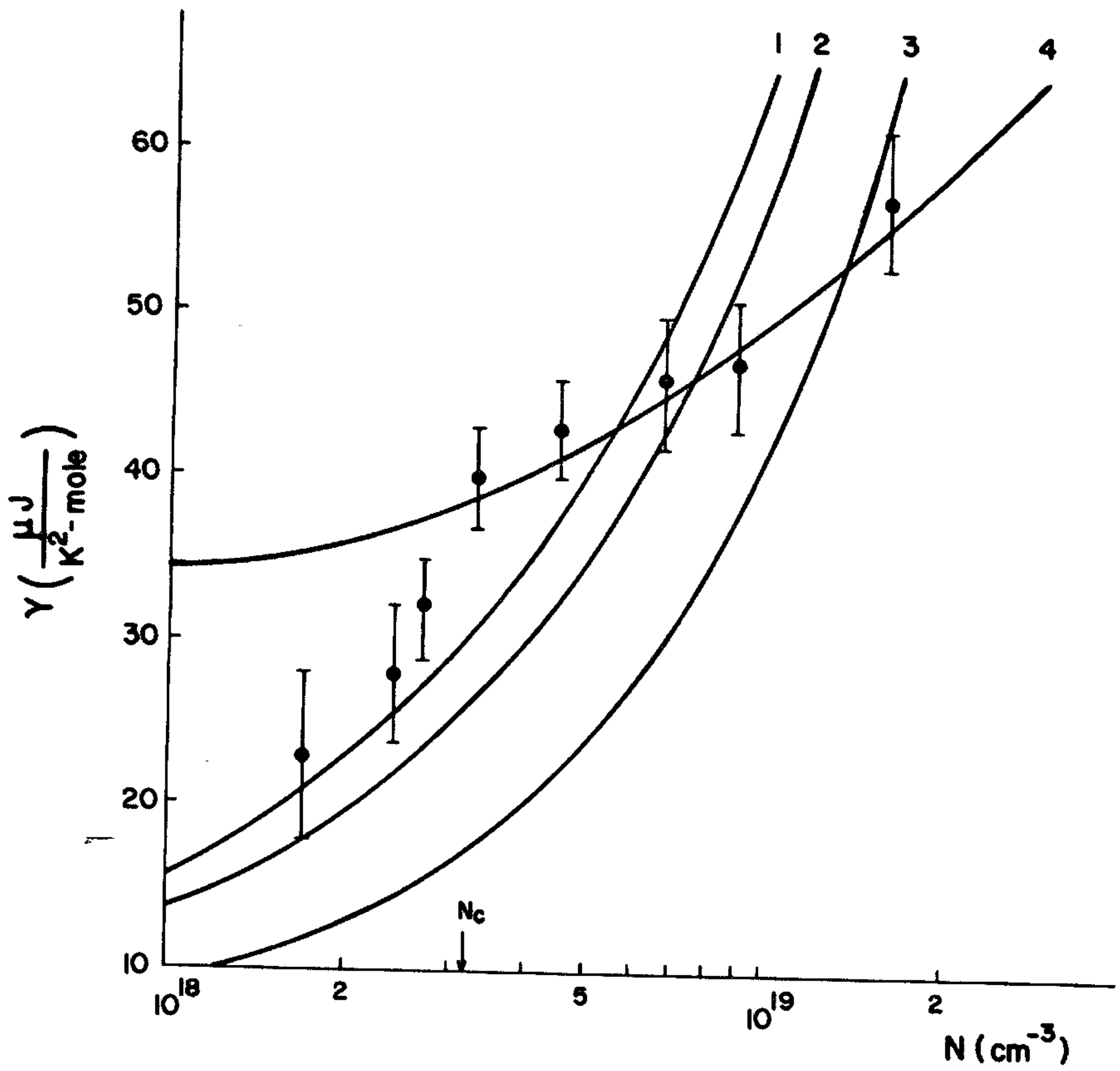

Fig. 2 M. Fabbri et al

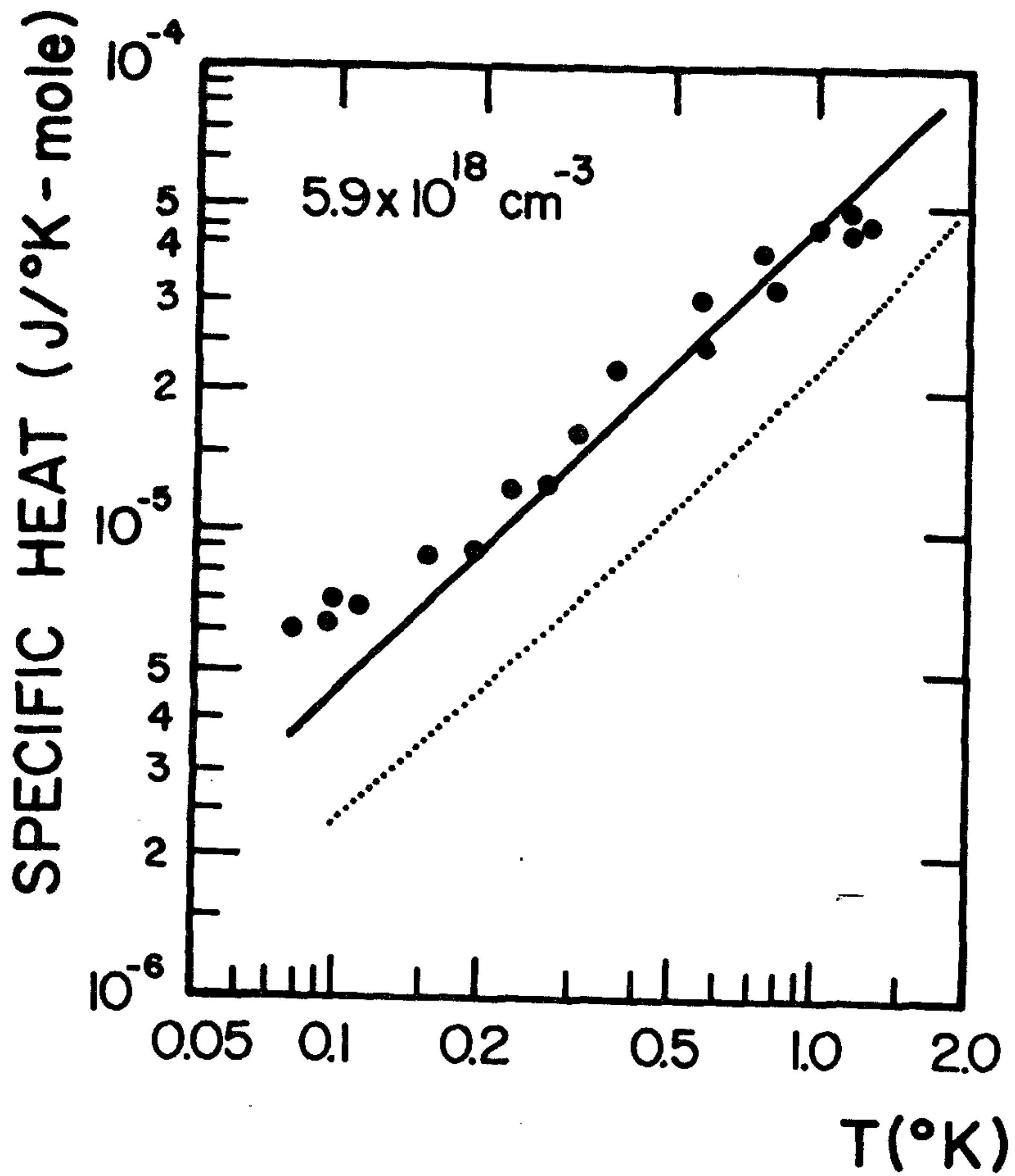

Fig. 3 M. Fabbri et al