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DIFFUSION AND SOLUBILITY OF Zn IN GaSb* +

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ABSTRACT

This work repports on experimental results of chemical diffusion and of diffusion under isoconcentration conditions of Zn in p-type GaSb ($p = 10^{17}$ at cm^{-3}) obtained by radioactive tracer method. The chemical diffusion experiments, which lasted from 17 to 42 hours, were performed in the temperature range 560°C to 640°C. For isoconcentration experiments of levels of $4,5 \times 10^{20}$ and 6×10^{20} atoms per cm^3, performed at 560°C and 580°C and diffusion times of 40 and 20 hours, we obtained diffusion coefficients $D = 1,8 \times 10^{-11}$ and $D = 8 \times 10^{-11}$ cm^2 s^{-1}, respectively. It has been found that the diffusion coefficients depend linearly on concentration. The diffusion coefficient measured under conditions of isoconcentration is larger than the value obtained for chemical diffusion. The solubility of Zn in GaSb has also been studied in the temperature range from 540°C, a value of 93eV being obtained for the heat of solution. The maximum concentration $C_{Zn} = 1,1 \times 10^{21}$ cm^{-3} is found for T = 630°C.

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INTRODUCTION

The diffusion of zinc in III-V compounds presents an anomalous behaviour, the diffusion coefficient showing a dependence on concentration. [1-4] Of these compounds, the least studied, from this point of view, is GaSb, on which only three investigations have been published.[5,6,7] In a previous work[5], we have measured by the electrical conductivity method the chemical diffusion coefficient of Zn in GaSb which has been found to be concentration dependent, the diffusion occurring through the same mechanism as in other III-V compounds.

In this work we have investigated chemical diffusion and diffusion under isoconcentration conditions of Zn, as an impurity, in GaSb by radioactive tracer methods. We have also conducted measurements of the solubility of Zn in GaSb by both radioactive and electrical conductivity methods. The diffusion measurements were made in the temperature range of 560ºC to 640º while the solubility measurements were obtained in the range of 540º to 640ºC.

EXPERIMENTAL

For chemical diffusion measurements we used p type GaSb ($p \simeq 10^{17}$ at-cm^{-3}). For measurements of diffusion under isoconcentration conditions, GaSb doped with during growth was used. All samples were cut perpendicular to the pulling axis.

The experimental techniques of the diffusion has been described elsewhere. For isoconcentration measurements radioactive Zn^{65} was diffused in its saturated vapor phase at temperatures that range form 560ºC to 640ºC and diffusion times between 17 and 42 hours. In order to prevent stoichiometric variations, the possible formation of compounds like ZnSbGa on the sample and other unwanted effects caused by evaporation of antimonium, an excess pressure of Sb has been kept during the diffusion

process.

The diffusion profile was obtained by grinding off sucessive layers and measuring the activity of the material removed. The thickness of the layers removed was measured by weight difference.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the variation of the concentration in Zn^{65} for several temperatures and diffusion times. It is apparent that the distribution of Zn^{65} in p-type GaSb cannot be represented by an error function in the range 560ºC to 640ºC. One notices a sudden change in the concentration gradient, a fact also observed by Gooch[1] in the diffusion of Zn in GaAs. This effect, can be explained by the difference in diffusion speeds between ionized and non-ionized states of Zn in the lattice, the ionized atoms having a stronger interation with the lattice will be slower. The number of ionized atoms will depend on the position of the Fermi level which will vary with the total zinc concentration, hence causing a varying ratio of ionized to non ionized atoms.

The curves were not analyzed, as in ref. 5 and 7, applying the Boltzmann-Matano method. We present, however, in figure 2 for the sake of comparison, the carrier and Zn^{65} profiles obtained for the same sample. The fact that two curves are displaced accounts for the results previously obtained by us [5] which show D varying lineraly with concentration in the region 3×10^{18} to 10^{19} Zn atoms-cm^{-3}, while Blashku[7] finds linearity in the region 10^{19} to 10^{20} Zn atom-cm^{-3}.

In isoconcentration experiments the electric field due to the concentration gradient, which slows down the diffusion, is eliminated. The total concentration of Zn is not altered since, at the temperature of diffusion, the solution of Zn in GaSb is saturated and the diffusion of Zn^{65} occurs through isotopic exchange,

which does not alter the overall Zn concentration.

Fig. 3 shows the diffusion profiles for 560ºC and 580ºC and diffusion times, respectively, 40 and 20 hrs. The full lines correspond to error functions with $D = 1.8 \times 10^{-11}$ and $D = 8 \times 10^{-11}$ cm^2 sec^{-1}, for levels of isoconcentration of 4.5×10^{20} and 6×10^{20} atoms per cm^3, respectively. On the surface one notices a clear deviation from the erfc law, which shows that in this region the isoconcentration conditions are not met, a fact to be expected due to the large number of vacancies which are formed on the surface of the crystal. The results are agreement with what Blashku[7] found for isoconcentration conditions at 560ºC, 5×10^{19} atoms per cm^3, which gives a diffusion coefficient $D = 10^{-11}$ cm^2 sec^{-1}. We also show in figure 3 a profile of a chemical diffusion runs for T = 580ºC and t = 20hours. One can see the influence of the concentration gradient on the diffusion mechanism.

SOLUBILITY OF ZINC IN GaSb

Starting from the diffusion profiles obtained by the radioactive tracer technique it is possible, by extrapolation to $x = 0$, to obtain a solubility curve for Zn in GaSb as a funtion of temperature. For each temperature a series of measurements was carried out, varying the diffusion times so that greater precision was assured in the determination of the surface concentration. For each temperature the concentration on the surface is the same which shoes that the condition on the surface were quite reproducible, and that the conditions of saturation was attained.

Figure 4, curve b, shows the variation of solubility of Zn as a funtion of temperature. Between 540ºC and 640ºC the results can be represented by the relation

$$C_{Zn}\ (cm^{-3}) = 1.7 \times 10^{26}\ \exp(-.93/kT)$$

The value of .9 eV for the heat of solution is common to all compounds III-V except InSb according to (8). The maximum concentration, C_{Zn} = 1.1×10^{21} cm^{-3} is found for T =630ºC. For higher temperatures there is a decrease in the solubility. This can be accounted for if one considers the simultaneous action of the temperature and of the coefficient of segregation k. At low temperatures, for large dilutions, k does not depend on the temperature, but as the melting point is approached, k becomes a decreasing function of impurity concentration, hence a large decrease in the solubility.

In the isoconcentration experiments, the level of the isoconcentration of the doped crystal was measured by Hall effect, which gives the number of charge carries but not the number of Zn atoms. In order to obtain the solubility of the carriers p_o as a funtion of temperature we extrapolated to the surface the profiles of the number of carriers. Fig. 4, a, shows the curve obtained. The difference between the two curves can be explained by the existence of neutral Zn atoms or by the presence of precipitates which can be formed depending on the speed of cooling.

CONCLUSIONS

The experimental results obtained in this work confirm the fact that, as for the other III V compounds, the diffusion coefficient of Zn in Ga Sb, as an impurity, depends on concentration. The isoconcentration diffusion coefficient is larger than for chemical diffusion. This difference is attributed to the electric field generated by the concentration gradient or by the junction p p^+ formed in p--type GaSb.

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FIGURE CAPTIONS

Fig. 1 - Chemical diffusion profiles of Zn^{65} in p type GaSb. Samples: C_2, 20h at 580ºC; 2a, 17h at 610ºC; g_1, 40h at 560ºK; D-1, 20h at 625ºC, G-2, 40h at 638ºC.

Fig. 2 - Chemical diffusion profiles given by measuring the Zn^{65} concentration (C_{Zn}) and the number of carriers, (p) in a sample diffused by 17h at 610ºC.

Fig. 3 - Profiles for isoconcentration of Zn. 1)-40 hours at 560ºC; 2)-20 hours at 580ºC; 2')-Chemical diffusion for the same conditions as in Fig. 2.

Fig. 4 - Solubility of Zn in p type GaSb. C_{Zn} is the total concentration of Zn. p is the number of carriers per cm^3.

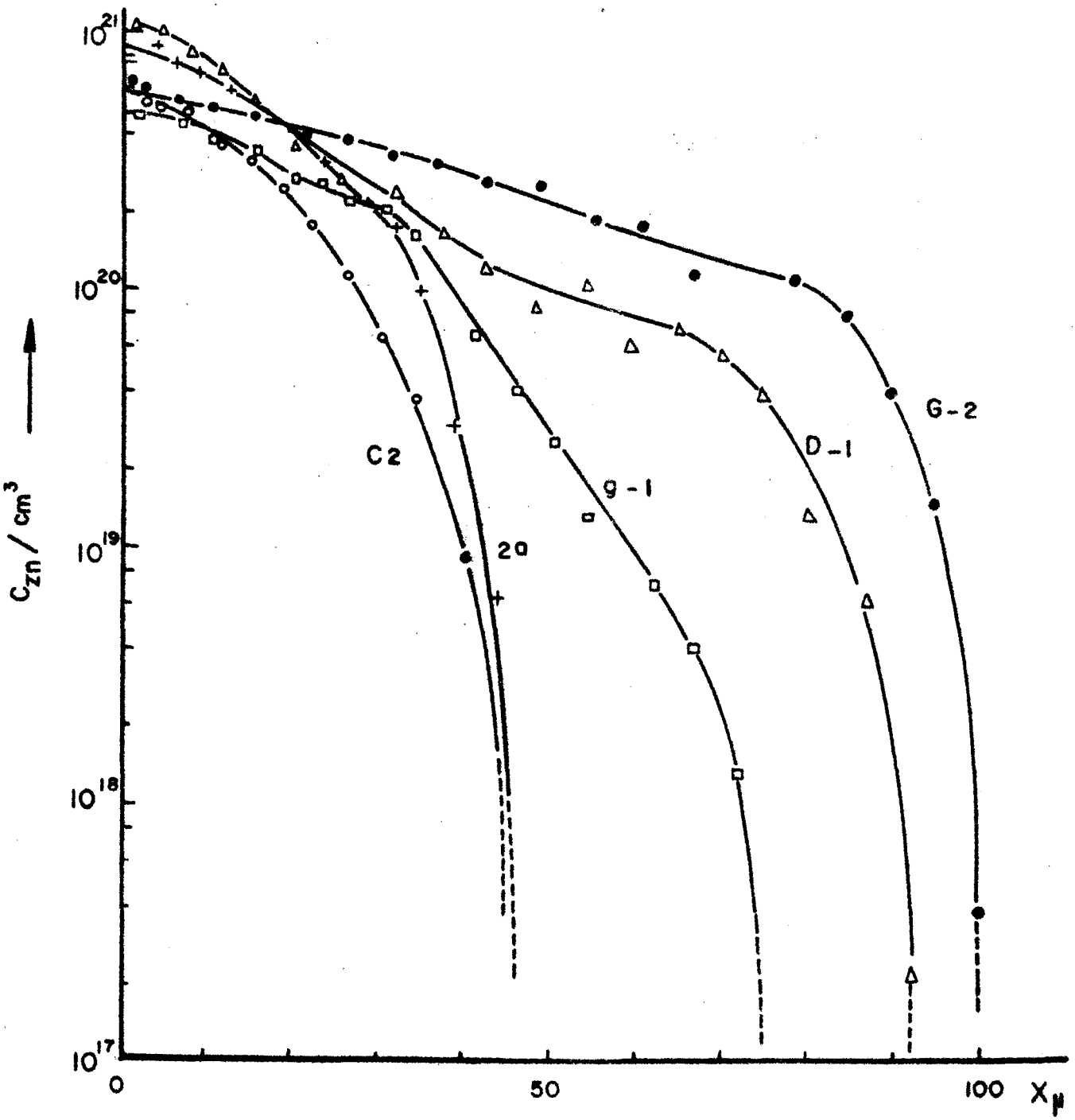

Fig. 1

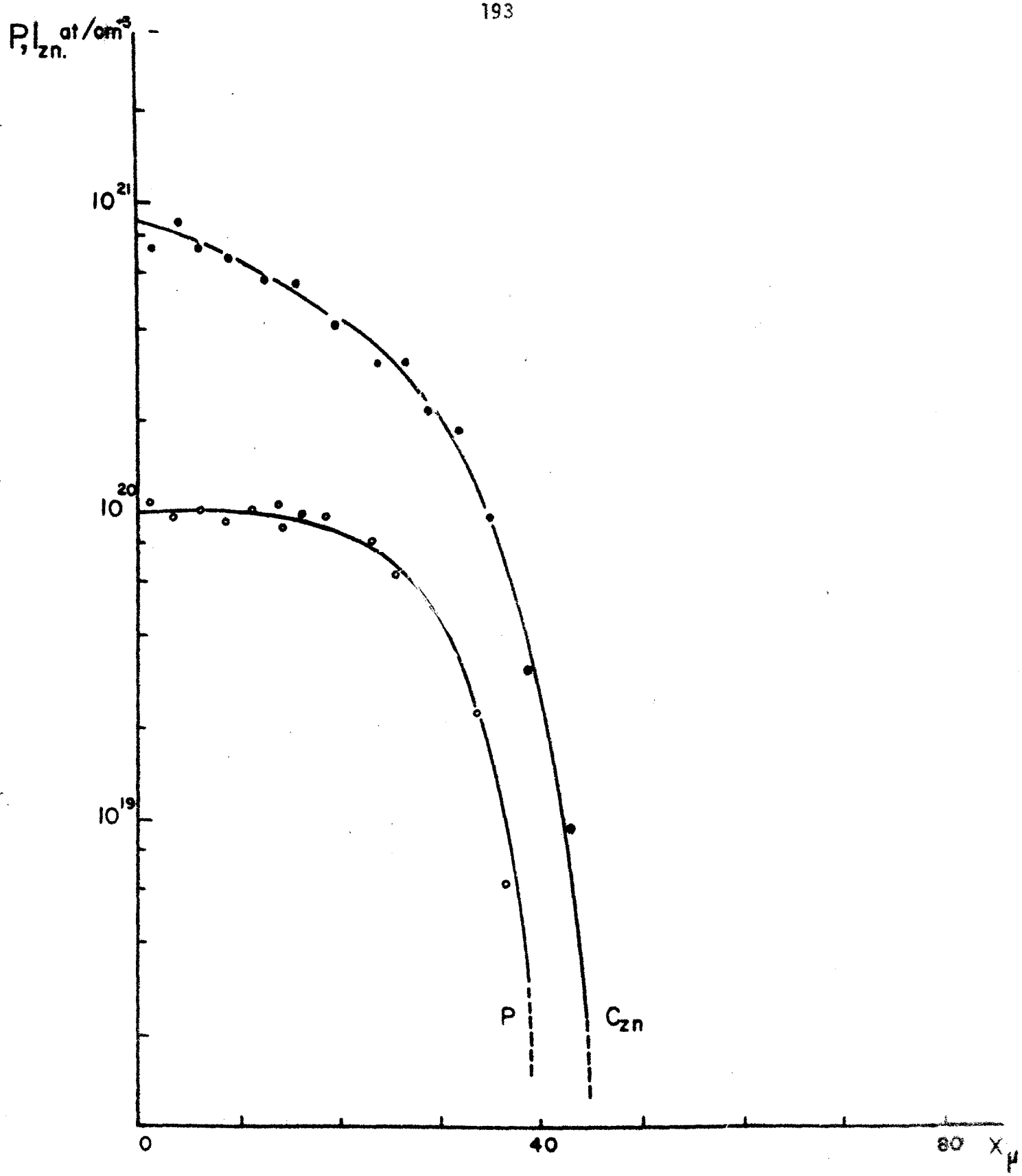

Fig. 2

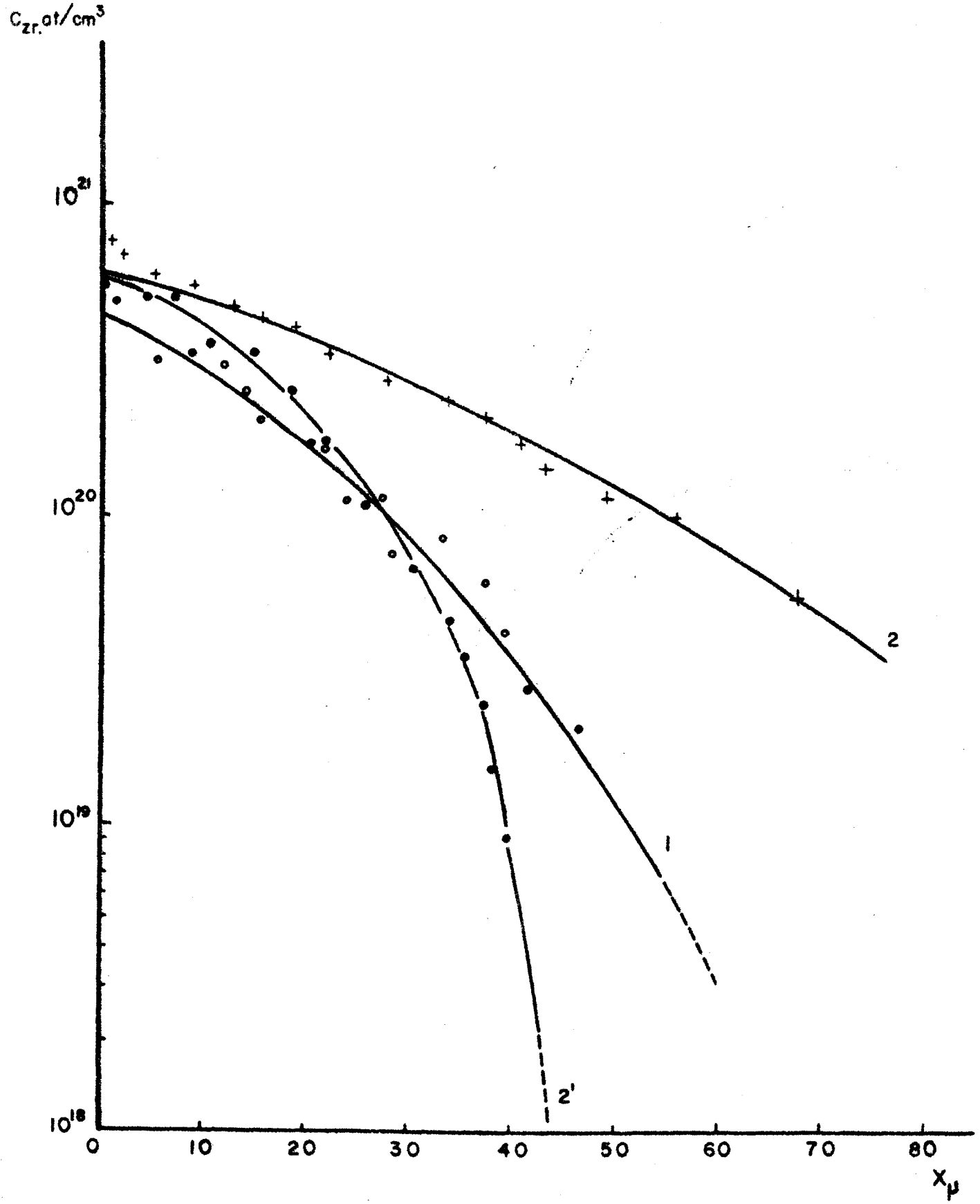

Fig. 3

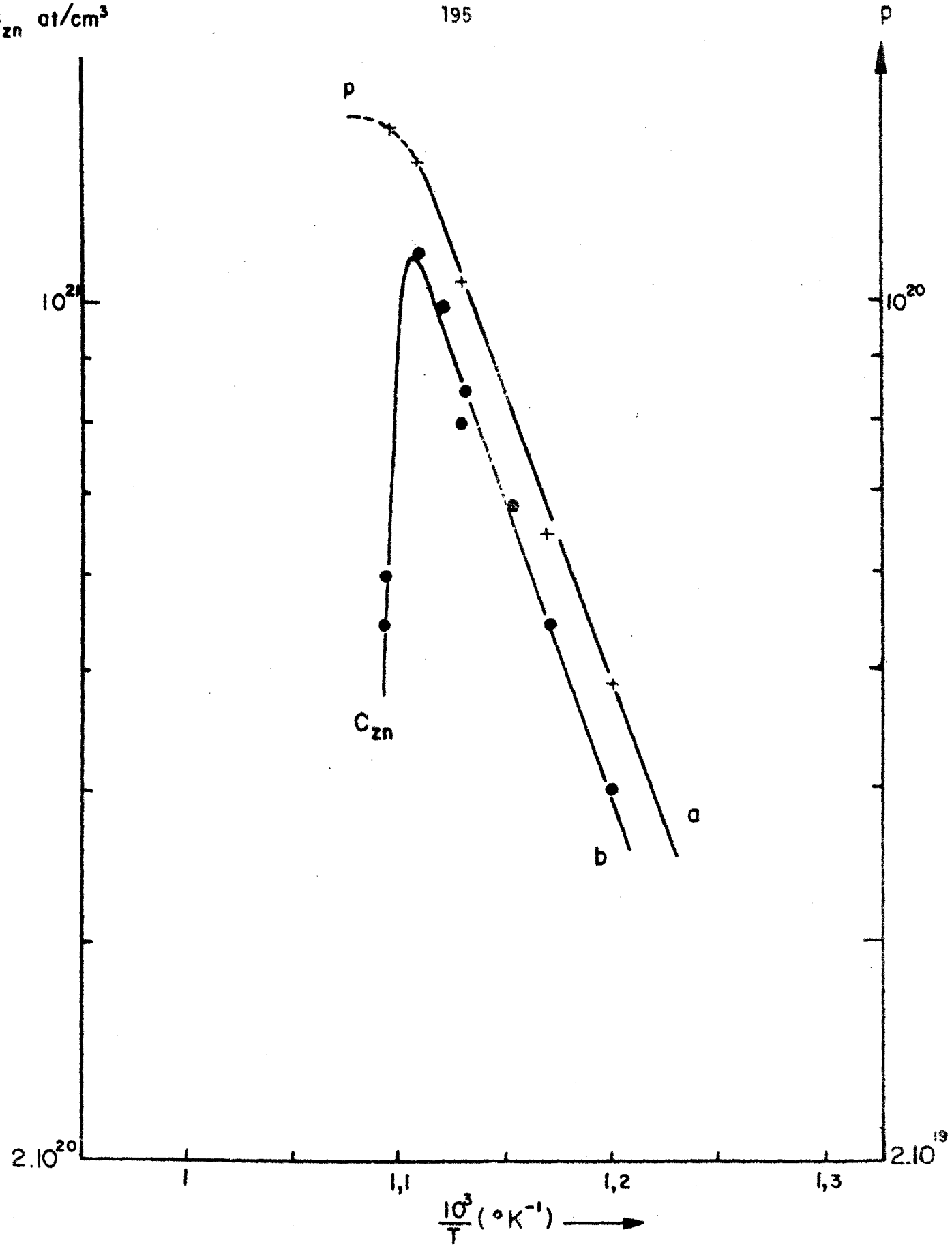
C_{zn} at/cm³
p
10^{21}
2.10^{20}
10^{20}
2.10^{19}
p
C_{zn}
a
b
1
1,1
1,2
1,3
$\frac{10^3}{T}$ (°K⁻¹)

Fig. 4

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