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MAGNETIC SUSCEPTIBILITY OF QN(TCNQ)$_2$

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ABSTRACT

The magnetic susceptibility of Qn$(TCNQ)_2$ was measured on single crystals and on powder (obtained by crushing) by static and ESR methods. The low temperature upturn is demonstrated to be due to chain ends, the susceptibility characteristic of infinite chains suggests a non-magnetic ground state. The temperature dependence of χ is qualitatively different from that observed in less conducting complex TCNQ salts.

АННОТАЦИЯ

Измерялась магнитная восприимчивость на монокристалле и прессованном порошке Qn $(TCNQ)_2$ статическим и ЭСР-методами. Доказано, что увеличение магнитной восприимчивости при низких температурах является следствием концов цепей. Магнитная восприимчивость, характерная для бесконечной цепи, указывает на немагнитное основное состояние. Зависимость от температуры по своему характеру отличается от наблюдаемой на плохопроводящих комплексных TCNQ солях.

KIVONAT

Qn$(TCNQ)_2$ mágneses szuszceptibilitását mértük egykristályon és /préseléssel nyert/ poron sztatikus és ESR módszerrel. Az alacsony hőmérsékletü növekedésről megmutatjuk, hogy a láncvégek következménye, a végtelen láncra jellemző szuszceptibilitás nem-mágneses alapállapotra utal. χ hőmérséklet függése jellegében különbözik attól, amit rosszul vezető complex TCNQ sókon figyeltek meg.

Opinions on the unusual properties of the well conducting charge transfer salts based on the organic acceptor tetracyano quindimethane (TCNQ) are still widely diverging. Quinolinium $(TCNQ)_2$, one of the best organic conductors has been variously claimed to be a metal[1] with negligible Coulomb correlations[2], a semiconductor having localized electron states even at room temperature[3] or undergoing a transition from disordered Mott-insulator to disordered metal at lower temperatures[4]. These concusions were reached partially on the basis of the behaviour of the magnetic susceptibility. The nearly temperature independent part observed above around 100°K is in broad agreement with a one dimensional metallic behaviour[3], and with that expected for a regular Heisenberg chain[3], available experiments were not able to distinguish between these two cases. The low temperature upturn observed in these salts was attributed to impurities or to chain end effects[1] and also to intrinsic behaviour due to inherent disorder[4]. We have performed high precision static susceptibility and low frequency (24 MHz) ESR experiments to try to distinguish between these descriptions. Qn$(TCNQ)_2$ was prepared according to Melby[5]. The salt was obtained in form of long needles having a blue-black colour[6], the Qn and TCNQ chains are parallel to the needle axis as confirmed by dc resistivity measurements. The static susceptibility and ESR measurements were performed on randomly oriented needles and on powder obtained by pressing. The measurement of the susceptibility by low frequency ESR is based on the Schumaker-Slichter technique[7]. However instead

of comparing the ESR and NMR signal intensities at all temperatures, the temperature dependence of the apparatus sensitivity was determined by measuring the temperature dependence of the fluor resonance signal intensity of teflon, the integrated ESR and NMR intensities of $Qn(TCNQ)_2$ were compared only at room temperature. Care has been taken to avoid saturation effects of the NMR signal.

The temperature dependence of the static susceptibility measured before (single crystal) and after (powder) crushing is shown in Fig. 1, the inset shows the low temperature part in log-log scale, corrected for the diamagnetic contribution (see below).

The temperature dependence of the susceptibility measured by ESR in shown in Fig. 2. Single crystals show a Lorentzian ESR line at all temperatures with a peak-to-peak width of the derivative signal 200 mG slighly increasing with increasing temperature, and the susceptibility was obtained by integrating the resonance curve. The ESR signal of a heavily crushed sampled consits of a sharp central component and long tails, the intensity of the central peak decreases, while that of the wings increases with decreasing temperature.

The difference of the magnitude of the susceptibility measured by the two methods is due to the diamagnetic con-

tribution of the susceptibility measured by a magnetic balance but not with ESR. A comparison of $\chi(T)$ shown in Figs 1 and 2 gives a temperature independent diamagnetic contribution $\chi_{dia} = -3.7$ emu/mole in good agreement with that calculated from Pascal's constants -3.5 emu/mole[1].

The increase of the static susceptibility due to crushing is evident from Fig 1, and strongly indicates that the low temperature upturn is due to effect of chain ends, as crushing the material reduces the average chain length. Below about 20°K, the susceptibility is fitted well with $\chi_{LT}(T) = AT^{-\alpha}$ in both cases (see insert of Fig 1) with $\alpha = 0.65$ and $A = 4.8\ 10^{-3}$ and $5.5\ 10^{-3}$ emu/mole °K respectively. The functional dependence on the temperature is the same than that found by Bulaevski et al[8]. This particular power law results from a model, where some of the spins are weakly coupled to the surroundings, and the distribution of the coupling strength goes as $\omega^{-\alpha}$, where α is a phenomenological parameter. The good agreement with the experiments indicates, that the origin of the power law is correcty identified by Bulaevski et al, however the different magnitude of the upturn obtained on samples before and after crushing demonstrates, that it is due to spins localized at ends of the TCNQ chains, and is not an inherent property of the material.

The evaluation of that part of the susceptibility, which is characteristic to an ideal $Qn(TCNQ)_2$ salt with infinite chains depends heavily on the high temperature contribution of the chain ends. In the wiev of the possibility of having a transition from localized to delocalized electron states any a'priori substraction procedure is amiguous. We have assumed, that the low temperature power law extends to high temperatures and substracted it from the measured susceptibility. The temperature dependence of the inherent susceptibility $\chi(T) - \chi_{LT}(T)$ obtained for single crystals and for powder is shown in Fig 3. The good agreement between the two sets of points - in wiev of the large difference of the total susceptibility shown in Fig 1 - strongly supports this substraction procedure.

The behaviour displayed in Fig. 3 indicates a nonmagnetic ground state with a gap in the magnetic excitation spectrum, similarly to that observed for other complex TCNQ salts[3]. As $^{n}/_{N} = {}^{1}/_{2}$ where n and N is the number of electrons and TCNQ molecules respectively, in the absence of observable alternation of distances between the TCNQ molecules[9] the most likely explanation of the nonmagnetic ground state is the formation of singlet pairs separated by two neutral TCNQ molecules, as suggested by Beni et al[10]. This picture obviously neglects the disorder introduced by the asymmetric donor molecules, however if the

singlet binding energy is larger than the random potential, a nonmagnetic ground state is reatined. The temperature dependence of χ shown in Fig. 3 is distinctively different from that expected for excitations will well defined energy. In complex salts excitations involving triplet states, or two independent spins are of importance. For singlet-triplet excitations $\chi(T) = (2\mu_B^2/kT) \times e^{-J/kT}(1+3e^{-J/kT})$, where I the echange ocnstant. This expression gives a good overall description of the susceptibility observed in less conducting TCNQ salts[1], extensions of this model including triplet exciton band[10] modify only slightly the temperature dependence. When two independent spins are excited $\chi(T) = (2\mu_B^2/kT)\, e^{-J'/kT}(1 + 4e^{-J'/kT})$ I' the energy required to excite two independent spins. In Fig. 3 both expressions normalized to the high temperature susceptibility are shown for comparison. In contrast to the strongly peaked susceptibility obtained from both models, the smooth increase of the measured susceptibility suggests either a distribution of excitation energies due to the random disorder, or a strong wave vector dependence of I or I' i.e. an excitation band wide compared to the average excitation energy.

Finally we mention, that the narrow ESR line points to delocalized electron states with rapid hopping. In the strong exchange narrowing limit the linewidth is given by $\Delta\omega = \Delta\omega_o^2 \tau_c$ where τ_c the correlation time determined by the exchange and/or hopping frequency of the excitations,

$\Delta\omega_0$ the full dipolar linewidth. In the former case $\tau_c \sim \hbar/J$ where J is the exchange coupling. Narrow (of the order of half Gauss) ESR lines are observed[11] in cases of strong exchange constant, of around 0.3 eV. For Qn$(TCNQ)_2$ J, although not a well defined quantity should be considerably less than the above value, thus exchange alone would lead to a much larger linewidth then the measured value. Therefore the rapid hopping should be responsible for the observed narrow ESR line. With $\Delta\omega_0 \sim 3 \times 10^{-19}$ sec^{-1}, ΔH = 200 mG gives a hopping frequency $\tau_c \sim 10^{-13}$sec^{-1}. This value is between that expected for phonon assisted hopping $\tau_c \sim 10^{-12}$sec and for a narrowband metal $\tau_c \sim 10^{-14}$sec. A similar conclusion has been reached by measuring the nuclear spin lattice relaxation time[2] T_1, which gives a hopping frequency again of the same order of magnitude at room temperature.

In conclusion we have demonstrated, that chain ends play an important role in the temperature dependence of the measured susceptibility of Qn$(TCNQ)_2$. The ground state of the ideal - infinitely long - TCNQ chains is that of a non-magnetic insulator, and $\chi(T)$ is qualitatively different from that observed in less conducting complex salts of TCNQ.

The above interpretation is qualitatively different from that asserted by other authors[1,4,13]. We believe however that the consistensy of our substraction procedure obtained on two different samples favours our conclusion about the temperature dependence of the susceptibility.

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N calculated 23.4 %, found 23.4 %

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FIGURES

Fig. 1 Temperature dependence of the static susceptibility. The inset shows $\chi(T)$ in log-log scale

Fig. 2 Temperature dependence of the susceptibility measured by ESR method. The dotted line is the static susceptibility after correction for dia-magnetic contribution.

Fig. 3 Temperature dependence of the inherent susceptibility of Qn(TCNQ)$_2$. Dotted line: singlet-triplet model I = 5.2 10^{-2} eV. Full line: singlet-two independent spin excitation I' = 4.75 10^{-2} eV.

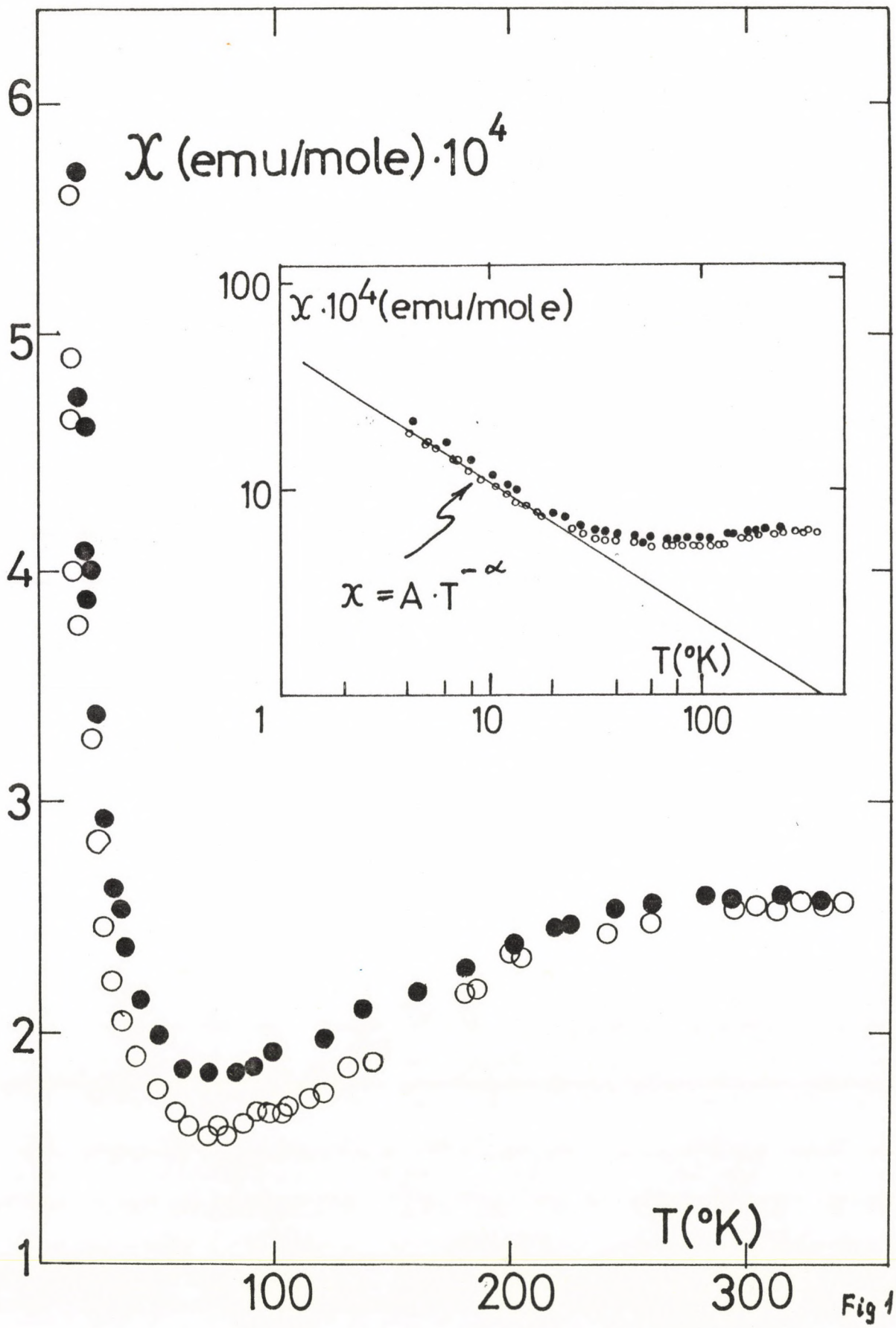

χ (emu/mole)·10^4
6
5
4
3
2
1
100
200
300
T(°K)
χ·10^4(emu/mole)
100
10
1
10
100
T(°K)
χ = A·T^-α

Fig 1

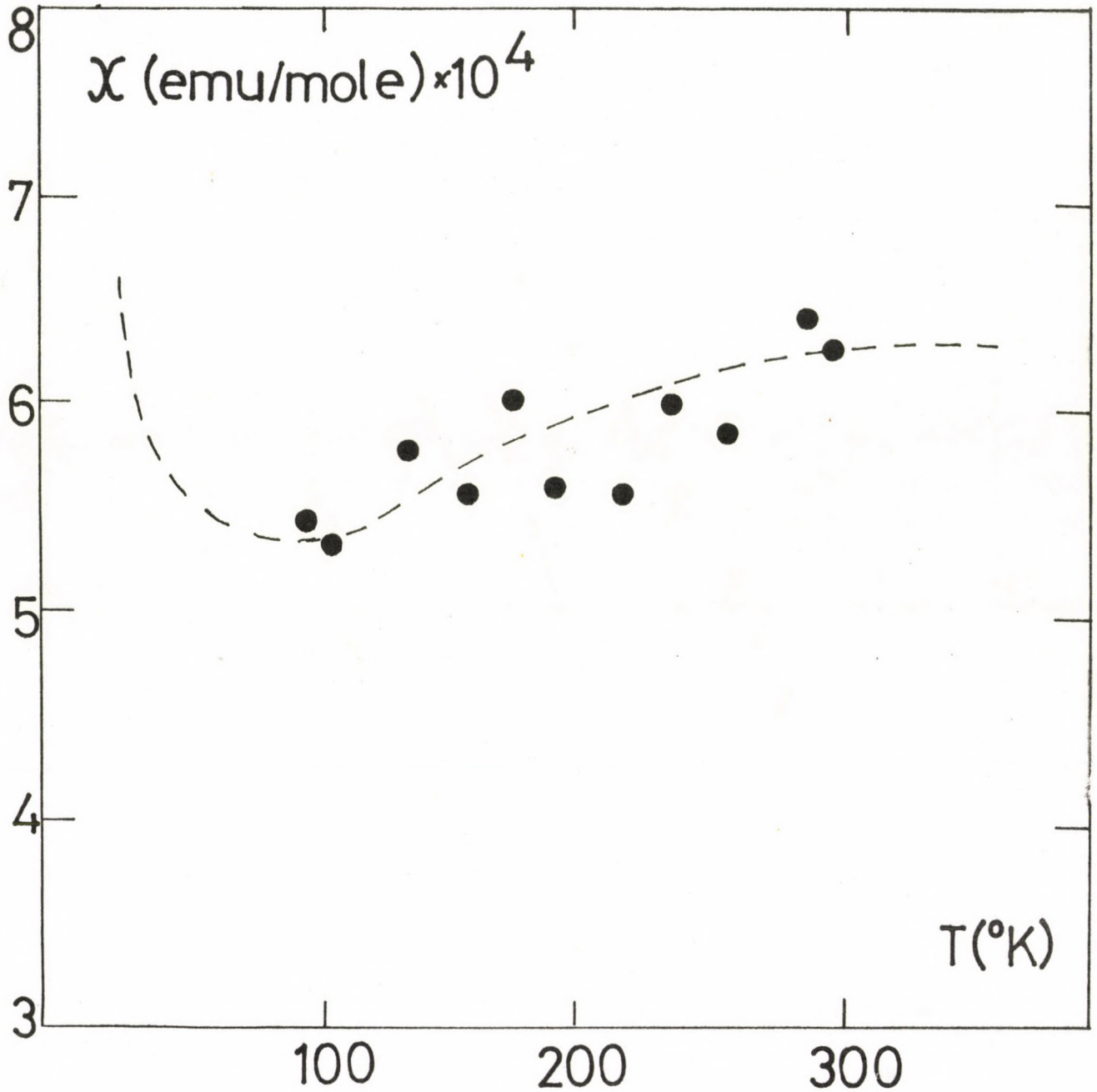


Fig 2.

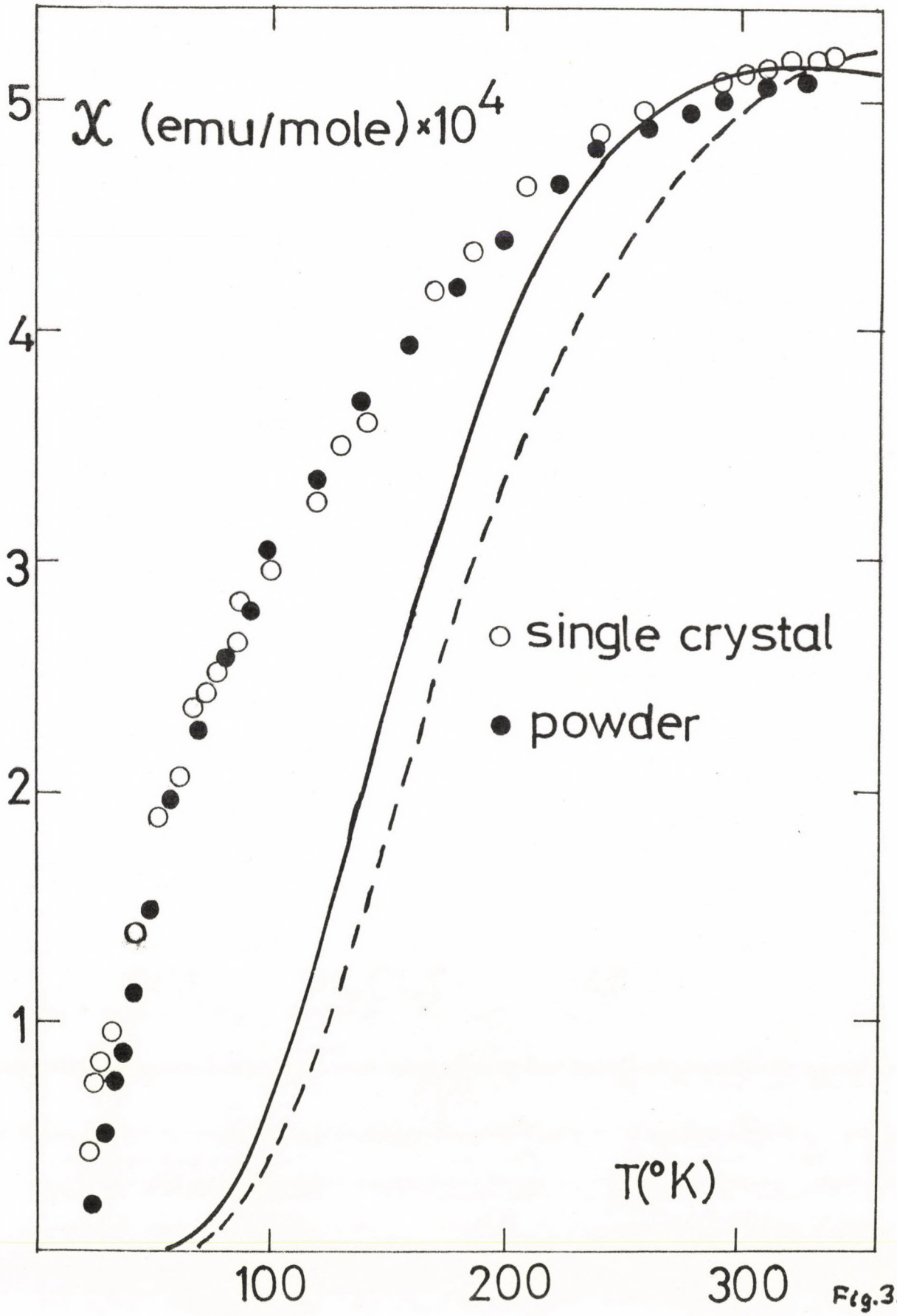
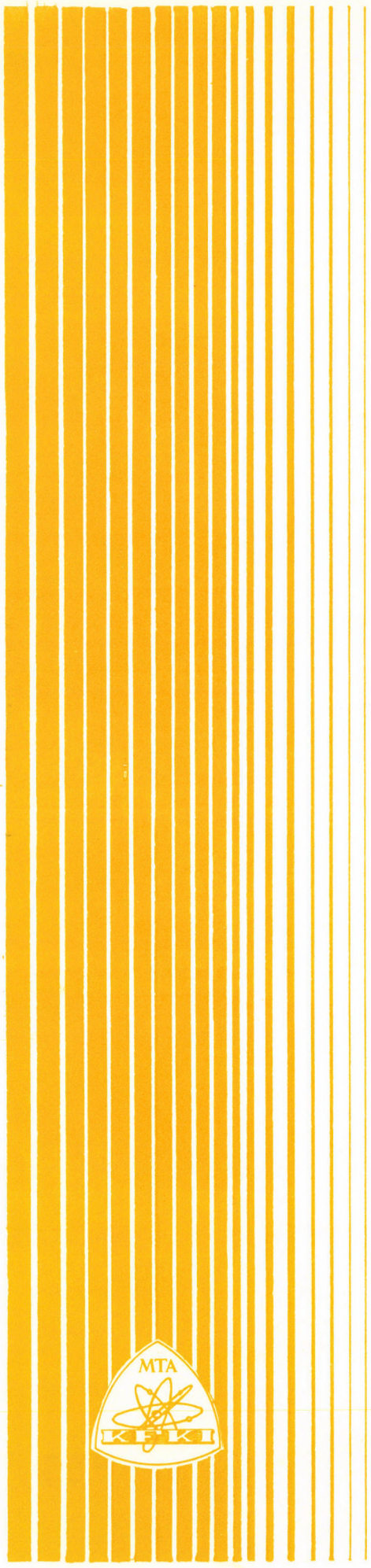


Fig.3.

62.111



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