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ABSTRACT

The behaviour of AgCl and AgBr is contrasted with that of fluorite-type crystals, which also are Frenkel conductors at low temperatures but undergo a diffuse transition to a superionic phase before melting. Concentrating on AgBr for which the relevant defect parameters are better known, a Debye-Hückel model for the interactions between defects, modified for saturation of screening at high defect concentrations, is used to show that both Frenkel and Schottky disorder are present and rapidly increasing with temperature in the hot solid, with the Schottky component rapidly overtaking the Frenkel component. It is suggested that this defect behaviour frustrates a superionic transition and leads to melting accompanied by an anomalous ionic conductivity in the pre-melting region. The model is tested by a comparison with data on the Frenkel defect concentration in superionic PbF_2.

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I. INTRODUCTION

The silver halides far from melting are typical examples of moderately good ionic conductors, with an intrinsic conductivity σ of the order of $10^{-4} \div 10^{-3}$ $(\Omega cm)^{-1}$. The relatively high conductivity is due to the presence of an appreciable concentration of cationic Frenkel defects.

At low temperatures AgI differs from AgCl and AgBr in that its co-ordination is tetrahedral (wurtzite (β) or zincblende (γ) structure), while the co-ordination in AgCl and AgBr is octahedral (rocksalt structure). At 420K AgI undergoes a structural transition to an open structure (bcc lattice of iodine ions) where the silver ions are disordered over many sites and the material assumes the properties of a good superionic conductor. The mechanism which drives such a transition has not yet been explained quantitatively but is understood as being associated to the special bonding properties of AgI (mixed ionic-covalent bonding), in particular to the extremely weak bond-bending forces (Phillips 1976) which are also responsible for soft-bending modes. This characteristic is not exhibited by AgCl and AgBr, which are thus inhibited from becoming superionic conductors of the type of AgI.

However, AgBr and to a less extent AgCl exhibit very interesting anomalous properties in the ionic conductivity σ as a function of temperature (Aboagye and Friauf 1975), starting at temperatures approximately 100÷150 degrees below the melting point T_m (T_m = 728K for AgCl , T_m = 701K for AgBr). In the case of AgBr, σ is of the order of 10^{-1} $(\Omega cm)^{-1}$ at these temperatures and rises to practically $1(\Omega cm)^{-1}$ at the melting point. The cationic diffusion coefficient becomes correspondingly large.

Such a qualitative behaviour reminds us of the case of the fluorites (see e.g. Catlow 1980), which are also moderate Frenkel-type conductors at low temperatures and attain high conductivity at temperatures of a few hundred degrees below melting to deserve the name of superionic conductors. These systems actually present a diffuse phase transition to the highly conducting phase. The occurrence of such a transition in the fluorites has recently been associated with an instability in an assembly of Frenkel defects interacting essentially via Coulomb forces (March, Richardson and Tosi 1980), the transition temperature scaling nicely with the value of the formation energy of a Frenkel defect.

Now the question arises: why are AgCl and AgBr not superionic conductors of the type of the fluorites? To answer this question we have studied in detail the case of AgBr, where the relevant parameters are better known.

As a first answer to this question it might seem natural to suppose that the reason for the lack of a superionic phase is that a superionic transition is somehow superceded by melting through competing disordering effects on both sublattices. This was in fact the idea which motivated the present work. The purpose of this paper is to investigate the above hypothesis in a quantitative model.

II. POINT DEFECTS AND ANOMALOUS CONDUCTIVITY IN AgBr

The anomalous conductivity of AgCl and AgBr has been studied in detail over many years (for a review see Friauf 1977). Starting from the picture of an assembly of interacting Frenkel defects, Lidiard (1957) suggested that the anomaly is due to long-range Coulomb interactions between the defects, in the framework of the Debye-Hückel-Lidiard (DHL) theory. This point of view was shared by several workers. In particular Aboagye and Friauf (1975) treated in detail the assembly of Frenkel defects within the DHL theory and considered also the presence of divalent impurities and their complexes with cation vacancies. They found a well-defined set of intrinsic parameters for the Frenkel defect through an accurate fit of the conductivity data at low and intermediate temperatures. Extrapolation to higher temperatures did not allow them however to reproduce with these parameters the $\sigma(T)$ anomaly, at temperatures above 550K for AgBr. The discrepancy was sufficiently large to make them invoke effects other than Coulomb forces as responsible for a decrease in the Gibbs free energy energy of formation of the defects. One such effect is a softening of the lattice, which is expected to play a role as the temperature approaches T_m.

Indeed lattice softening has been suggested by other workers (Teltow 1949, Schmalzried 1959, Müller 1967) to be the main mechanism responsible for the $\sigma(T)$ anomaly. However the question of the temperature dependence of the formation energy has not yet received a definite quantitative answer (Friauf 1977). Recent data on the diffusion of alkali ions in AgBr, which show a regular Arrhenius behaviour, have brought renewed interest to this subject (Cardegna and Laskar 1981).

In all the above-mentioned studies the presence of Schottky defects has been neglected. On the other hand, Schottky defects have been invoked in the past to explain the change of several properties other than the ionic conductivity near melting (Kanzaki 1951, Kobayashi 1952, Kurnick 1952, Lawn 1963).

Recently D'Aguanno (1979) and Conti, D'Aguanno and Tavares (1982) have analyzed the available experimental evidence on conductivity, diffusion, and NMR in AgBr basically with the same approach as Aboagye and Friauf but allowing explicitly for the presence of Schottky defects. In this way they have also been able to obtain an estimate of the intrinsic parameters of this defect. Their main results are as follows:

i) The comparison of the defect parameters(see Table I) indicates that the formation energy E_F of a Frenkel defect is sufficiently smaller than the formation energy E_S of a Schottky defect ($E_S - E_F \simeq 0.5$ eV) to account for the low temperature behaviour of AgBr as a Frenkel conductor, but the formation entropy S_S is large enough ($S_S \simeq 2S_F$) to discount models based only on Frenkel defects at temperatures above roughly 600K;

ii) An account of Schottky defects in an extrapolation into the high temperature region only slightly improves the agreement with experimental data on conductivity.

With this background information on the defect state of AgBr at various temperatures we proceed below to discuss the thermodynamic state of an assembly of interacting Frenkel and Schottky defects.

III. DEBYE-HÜCKEL INSTABILITY IN A MIXED FRENKEL-SCHOTTKY CONDUCTOR

In the following calculations we consider a mixed assembly of Frenkel and Schottky defects, treating for the moment their interactions by the simple Debye-Hückel theory that we shall later have to transcend. Our main concern is to understand the possible reasons why AgBr, unlike fluorite-type Frenkel conductors such as CaF_2, PbF_2 and $SrCl_2$, does not possess a high temperature superionic phase. We are not interested in an accurate fit of the ionic conductivity at high temperatures, which would involve an explicit dependence of all the parameters on temperature.

We use the values of D'Aguanno (1979) for the defect formation energies and entropies, and assume for the lattice parameter a and the dielectric constant ε their average values in the temperature range (500÷650)K (see Table I).

The equilibrium conditions for the mixed Frenkel-Schottky configuration are

$$x_i x_{vC} = 2 \exp(-g_F/k_B T) \quad , \qquad (1a)$$

$$x_{vA} x_{vC} = \exp(-g_S/k_B T) \quad , \qquad (1b)$$

where we write

$$g_F = g_F^0 - \mu_F = E_F - TS_F - \mu_F \qquad (2a)$$

$$g_S = g_S^0 - \mu_S = E_S - TS_S - \mu_S \quad . \qquad (2b)$$

In these equations we take

$$\mu_F = \mu_S = e^2\kappa/\epsilon \qquad (3)$$

with

$$\kappa^2 = \frac{4\pi e^2}{\epsilon v k_B T}(x_i + x_{vC} + x_{vA}) \quad . \qquad (4)$$

We have clearly neglected the difference between enthalpies and energies of formation and have used the Debye-Hückel expression for the shifts μ_F and μ_S in the chemical potential of the defects due to their interactions. The quantity v in the expression (4) for the Debye-Hückel inverse screening length κ is the volume per ion pair in the crystal, while the other symbols have their usual meaning. We also notice that electric neutrality restricts the concentrations of interstitials x_i, of cation vacancies x_{vC} and of anion vacancies x_{vA} to satisfy the relation

$$x_i + x_{vA} = x_{vC} \quad . \qquad (5)$$

Within the Debye-Hückel assumption of a unique screening length for all point defects, the ratio $\rho \equiv x_{vA}/x_i$ is independent of the defect interactions and only depends on the intrinsic formation free energies,

$$\rho \equiv x_{vA}/x_i = \frac{1}{2}\exp[(g_F^0 - g_S^0)/k_BT] \quad . \qquad (6)$$

This reduces the above equilibrium conditions simply to the equation

$$x_i(1+\rho)^{1/2} = \sqrt{2}\,\exp(-g_F/2k_BT) \qquad (7)$$

or equivalently

$$\frac{E_F}{2k_BT} - \frac{e^2\kappa}{2\epsilon k_BT} = \frac{S_F}{2k_B} - \ln x_i + \frac{1}{2}\ln\left(\frac{2}{1+\rho}\right) \quad , \qquad (8)$$

where

$$\kappa = \left[\frac{8\pi e^2(1+\rho)}{\epsilon v k_B T}\right]^{1/2} x_i^{1/2} \quad . \qquad (9)$$

This type of equation is known (Kurosawa 1957) to exhibit an instability at a certain temperature (T_c, say). The disorder is predominantly of Frenkel type if $\rho \ll 1$ for temperatures up to T_c and in such a case we call the instability for convenience a "Frenkel instability". If instead $\rho \gg 1$ at T_c we call it a "Schottky instability".

As suggested by March et al. (1980) we may associate to a Frenkel instability a tendency to form a superionic phase, in which one of the sublattices "differentially melts". Such a case is exemplified by the superionic fluorites, where the Frenkel defects predominate. In fact the difference $E_S - E_F$ of the intrinsic formation energies is a few eV (Lidiard 1974).

Following Kurosawa (1957) one could instead recognize in the case of a Schottky instability a tendency for the whole crystal to melt. This situation seems applicable to the alkali halides at temperatures near T_m.

AgBr presents an intermediate case, as indicated by the defect parameters in Table I.

3.1 Instability in AgBr

The solutions for x_i and x_{vA} in AgBr as functions of temperature are shown in Fig.1 (full lines). Our calculations yield an instability of the mixed defect assembly at $T_c = 669$K: at this temperature the defect concentrations are $x_i(T_c) = 1.2\%$ and $x_{vA}(T_c) = 3.5\%$, i.e. $\rho(T_c) \simeq 1/3$. In order to examine whether the instability is driven by the Frenkel or by the Schottky component, we have studied Eqs.(1a) and (1b) separately. With the parameters appropriate to AgBr an "isolated" Frenkel assembly would undergo an instability at $T_c^F = 680$K with $x_i(T_c^F) = 1.6\%$, whereas an "isolated" Schottky assembly would become unstable at a higher temperature $T_c^S = 715$K, with $x_v(T_c^S) = 2\%$.

Therefore the instability of the mixed assembly is still of the Frenkel type but the presence of the Schottky defects cannot be neglected. Their effect on the Frenkel component is to slightly destabilize it, decreasing the critical temperature and the critical concentration of Frenkel defects.

A crucial parameter in our model is the dielectric constant ϵ. Its large value has the effect of weakening the strength of the Coulomb interactions and therefore of sustaining the assembly of Frenkel defects against the Debye-Hückel instability up to temperatures where the concentration of Schottky defects becomes important.

The temperatures at which the instabilities of the two isolated components occur depend essentially on the values of the formation energies. Therefore we suspect that, whatever reasonable values one uses for E_F and E_S, T_c^F will be lower than T_c^S. By reasonable values we mean that they must be consistent with the experimental fact that x_{vA} does not exceed x_i for temperatures up to 600K. To investigate this point in more detail we have solved Eqs.(8) with another set of parameters, which favours the Schottky component at high temperatures but still has $E_F < E_S$. The solution is given in Fig.2, where the situation appears reversed relative to that of Fig.1. This would correspond to an instability of the whole crystal occurring before a Frenkel-type instability (i.e. melting before a superionic transition). However, the results in Fig.2 must be disregarded because they also imply $x_{vA} > x_i$ in the whole range of temperature of interest.

Thus the situation appears to be more complicated than one might at first envisage. Our result $\rho(T_c) \simeq 1/3$ perhaps indicates that AgBr at high temperatures is approaching a "frustrated superionic" state where Frenkel defects still predominate but the anion sublattice contains an appreciable amount of disorder. Our simple Debye-Hückel model does not have a solution for $T > T_c$ and therefore is not capable of describing how the defect system evolves above T_c. In the next section we extend the model to remedy this deficiency.

It is worth closing this section by remarking explicitly that the values of the various critical temperatures (T_c, T_c^F and T_c^S) that we have calculated above are all very close to the actual melting point of AgBr, $T_m = 701K$.

IV. EFFECT OF SATURATION IN THE SCREENING LENGTH

In recent work on superionic PbF_2 March and Tosi (1982) have argued, on the basis of neutron scattering data by the Harwell-Oxford group (Dickens, Hayes, Hutchings and Smith 1981, Hutchings 1982), that a major correction to the simple Debye-Hückel theory is to account for a saturation of the screening length with increasing concentration of defects. An examination of their results for the shift μ_F in chemical potential at various temperatures suggests that saturation of screening sets in rather rapidly once the screening length becomes of order of the distance of closest approach between defects. This type of behaviour, which is more abrupt than in the DHL extension of the simple Debye-Hückel theory, may arise from lattice effects not contained in continuum theories of electrolytes.

Here we follow this idea and introduce the saturation of the screening length in a manner that allows us to follow the evolution of the defect assembly at temperatures above T_c. In the lack of a proper theory we simply assume that saturation sets in abruptly at T_c and that the screening length maintains at higher temperatures the value κ_c^{-1} that it has attained at T_c. For AgBr this value is 3.13 Å, which is still somewhat larger than the distance of closest approach between defects. We return in the next section on PbF_2 to examine the consequences of this simple scheme against the neutron scattering data.

In the case of AgBr we have obtained the solutions for x_i and x_{vA} at temperatures above T_c from Eq.(8) with $\kappa = \kappa_c$. They are shown in Fig.1 (dashed lines) for temperatures up to 800K. Of course in a better treatment saturation of screening would be switched on less abruptly and the anomaly at T_c would therefore be smoothed out.

The main qualitative effect of the saturation of screening length is that of allowing a rapid growth of the concentrations of both Frenkel and Schottky defects. The concentration of Schottky defects grows more rapidly because of their larger formation entropy. A crossing point $x_{vA} = x_i$ occurs in our calculation at $T \simeq 780K$.

This is in our view the qualitative effect which could explain both the extra anomaly in the ionic conductivity of AgBr and the absence of a superionic phase through the rapid growth in the Schottky disorder overtaking the Frenkel disorder.

The actual temperature range where this rapid growth of the disorder occurs should be shifted downwards by roughly fifty degrees to make contact with the real situation in AgBr: an excellent result in view of our crude treatment. We lack of course a precise melting criterion at this stage but the crossing temperature may be taken as indicative.

V. SATURATION EFFECT IN PbF_2

In order to give more support to the idea of a saturation in the screening length and to the explicit results reported above for AgBr, we have applied the same scheme to the Frenkel-type superionic conductor PbF_2, where the values of $x_i(T)$ at high temperatures are approximately known experimentally (Hutchings 1982 and references given therein).

We now consider only Frenkel defects, with $E_F = 0.88 \div 1.0$ eV (Boyce, Mikkelsen and O'Keeffe 1977, Gordon and Strange 1978, Hwang, Lowe, Lau and Vaughan 1976, Liang and Joshi 1975), and we use for the dielectric constant the high temperature value $\varepsilon = 29$. The value of the entropy of formation is not known and we present calculations based on $S_F = 5.6\ k_B$, which is the value measured by Jacobs and Ong (1981) for CaF_2, and on the arbitrary choice $S_F = 7\ k_B$.

The results are shown in Fig.3, where the critical temperatures are also indicated. The temperature of the Debye-Hückel instability decreases from $T_c = 890$K to $T_c = 614$K on varying the defect parameters in the ranges indicated above. The actual transition temperature of PbF_2 to the superionic phase is 707K, i.e. intermediate between our results and in fair accord with curve 2.

By introducing saturation of screening we obtain a situation where the concentration of Frenkel defects is growing very fast with temperature. This qualitatively corresponds to the observed behaviour in the superionic phase of PbF_2.

The solution for $x_i(T)$ at $T \gtrsim T_c$ can now be written explicitly as

$$x_i(T) = n_i^{1/2} \exp(S_F/2k_B) \left[n_i^{-1/2} \exp(-S_F/2k_B)\, x_i^{(c)} \right]^{T_c/T} , \qquad (10)$$

where $x_i^{(c)} = x_i(T_c)$ and n_i is the number of interstitial sites per lattice site ($n_i = 1/2$ in the fluorite structure, in contrast to the value $n_i = 2$ adopted in Eq.(1a) for the rocksalt structure). It is clear from this expression that the formation entropy plays an important role in determining the rate of increase in the defect concentration above T_c, while the formation energy is also important in determining the value of T_c. The experimental data reported in Fig.3 include both true interstitials of Frenkel pairs and ions relaxed from their regular sites due to the presence of an adjacent interstitial in a concentration ratio of the order of $\frac{1}{3} \div \frac{1}{2}$; curve 2 thus seems closer to the real situation.

We should also remark that at high defect concentrations Eq.(1a) and consequently Eq.(10) should be corrected for the difference between the number of ions and the number of lattice sites. This introduces some saturation in the theoretical curves of Fig.3 at high temperature (e.g. curve 3 would rise to $x_i = 38\%$ rather than to $x_i = 46\%$ at $T = 1000$K), but we feel that this correction is minor compared with the basic uncertainty in the defect parameters over this wide temperature range.

VI. SUMMARY AND CONCLUDING REMARKS

AgBr is clearly a rather special case in that the intrinsic energy and entropy parameters for the formation of Frenkel and Schottky defects happen to be such as to allow appreciable amounts of both types of disorder as the crystal approaches melting. Both types of disorder increase rapidly with temperature in the hot solid, with the Schottky component rapidly overtaking the Frenkel component. In such a special case we have suggested that a possible diffuse transition to a superionic behaviour induced by the cationic Frenkel defects is frustrated by a simultaneous rapid disordering of the anionic sublattice due to Schottky defects. This leads to melting accompanied by an anomalous ionic conductivity in the premelting region. This is our tentative answer to the question posed in the title of the paper.

The model that we have used to illustrate this type of behaviour crucially relies on the role of the Coulomb interactions between point defects in the ionic material. The model is obviously very crude, but we believe that it contains the essential elements of the physical situation, i.e. screening of the Coulomb interactions described at very low defect concentrations by the Debye-Hückel theory and saturation of the screening effect once the screening length becomes comparable with the lattice parameter. We are at present unable to develop a microscopic theory of the saturation effect. We can draw some comfort however from the fact that the same model can be brought close to observation in the Frenkel-type conductor PbF_2.

The series of neutron experiments, both Bragg diffraction and quasi-elastic diffuse scattering, that have been carried out on PbF_2 have yielded not only quantitative data on the defect state in the superionic region but also suggested microscopic models for the defect state (Hutchings 1982). A similar experimental effort on AgBr would seem well worthwhile to shed light on its unusualy melting behaviour. Similar but less marked behaviours may also be expected for AgCl.

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Table I

Parameters used in the present calculations for AgBr +

E_F (eV)	E_S (eV)	S_F/k_B	S_S/k_B	a(Å)	ε
1.14	1.66	6.75	15.3	5.85	20

+ The values of the intrinsic defect parameters are from D'Aguanno (1979). The values of the lattice parameter a and of the dielectric constant ε are average values in the temperature range (500÷650)K. The values of ε(T) were measured by G.C. Smith (unpublished) and are reported by Friauf (1977).

FIGURE CAPTIONS

Fig.1 Concentrations of interstitials x_i and anion vacancies x_{vA} in AgBr as functions of temperature. Full lines up to T_c are obtained by the simple Debye-Hückel theory of Sec.III; dashed lines at high temperatures are obtained by including saturation of screening as discussed in Sec.IV. The parameters of the calculation are given in Table I.

Fig.2 The same as in Fig.1 with arbitrarily modified values of the intrinsic defect parameters (E_F = 1.2 eV, E_S = 1.6 eV, S_F = 6 k_B and S_S = 15 k_B).

Fig.3 Concentration of interstitials in PbF_2 as a function of temperature. The calculated curves (full and dashed lines have the same meaning as in Fig.1) are based on the following choices of defect parameters: curve 1, E_F = 1.0 eV and S_F = 5.6 k_B; curve 2, E_F = 1.0 eV and S_F = 7 k_B; curve 3, E_F = 0.88 eV and S_F = 7 k_B. The dark blobs and dash-dot curve are values for the fraction of anions leaving their regular lattice site obtained from the analysis of neutron scattering data (from Hutchings 1982). The critical screening lengths for the various theoretical curves are in the range $\kappa_c^{-1} \approx 2.0 \div 2.4$ Å^{-1}, to be compared with the near neighbour fluorine-fluorine distance d = 2.96 Å.

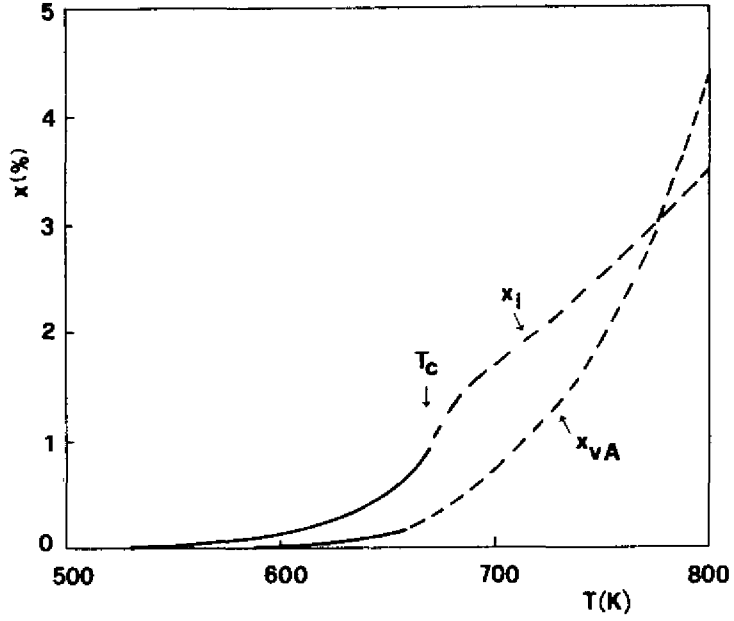
x(%)
5
4
3
2
1
0
500
600
700
800
T(K)
x_l
T_c
x_{vA}

Fig.1

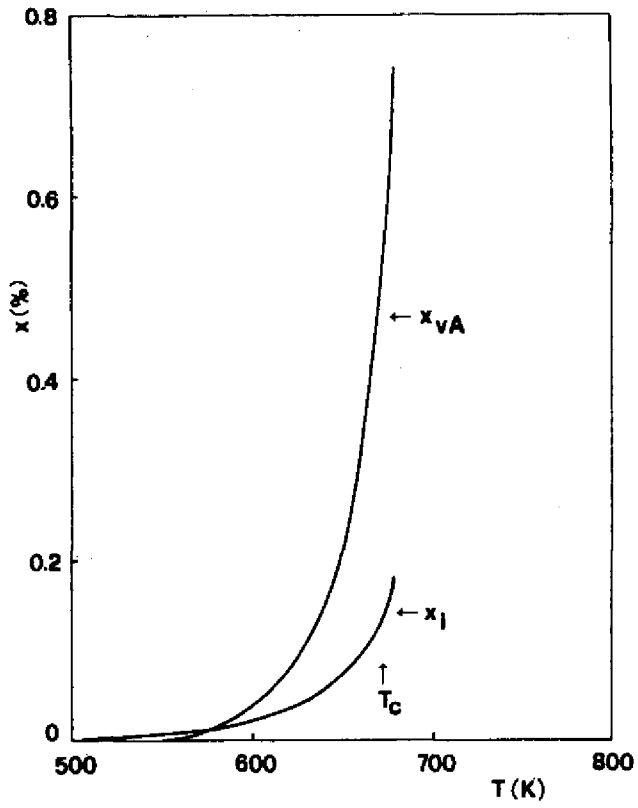
x(%)
0.8
0.6
0.4
0.2
0
500
600
700
800
T(K)
x_{vA}
x_l
T_c

Fig.2

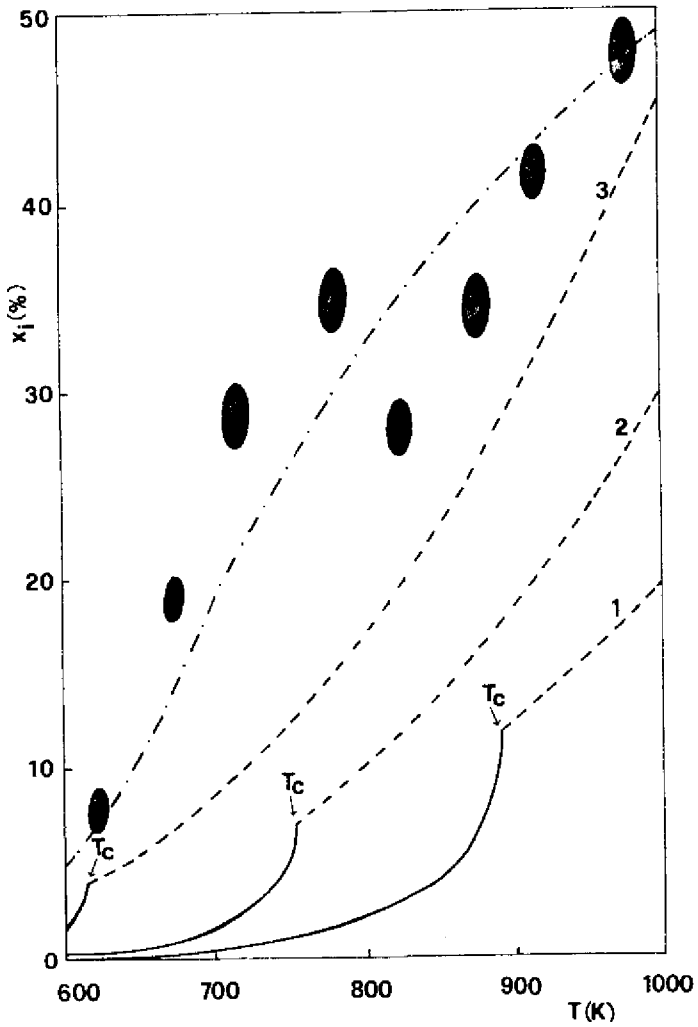

Fig.3

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