

Gradual solid electrolyte transition in $(C_5H_5NH)Ag_5I_6$

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In specific-heat measurements of the solid electrolyte $(C_5H_5NH)Ag_5I_6$, the disordering of the silver ions shows up in the form of a Schottky-type anomaly. A model calculation of the site occupancies of the Ag^+ ions and the excess specific heat reproduces the main features of the gradual transition to the solid-electrolyte state in this compound and proves that correlations between Ag^+ ions play an important role. Single-crystal conductivity measurements were carried out both along and perpendicular to the hexagonal axis. The large anisotropy of the conductivity at low temperatures ascertains that the motion of the Ag^+ ions through the channels provided by the c sites is much easier than the motion via pathways involving m sites. In addition, the specific-heat measurements show the existence of a second-order phase transition which is probably associated with the orientational disordering of the pyridinium ions. Finally, single-crystal conductivity results of $(C_5H_5NH)_3Ag_{18}I_{23}$ are presented which confirm the prediction of Geller *et al.* that this material is a two-dimensional solid electrolyte.

I. INTRODUCTION

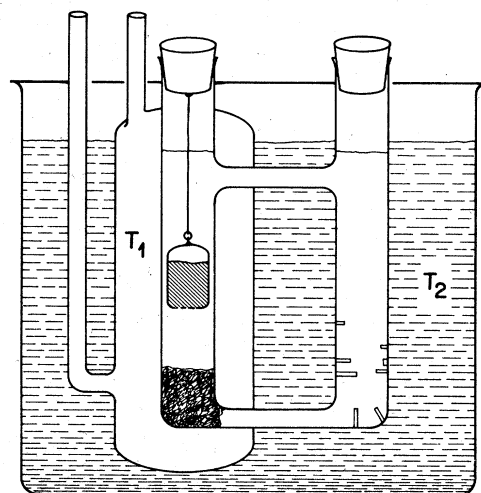
A recent study of Geller¹ and Geller and Owens² reveals that the solid electrolyte pyridinium-pentasilver-hexaiodide, $(C_5H_5NH)Ag_5I_6$, is unique amongst the large number of solid electrolytes on the basis of AgI, discovered to date.³ In most AgI-based solid electrolytes the transition, if one exists, to the solid-electrolyte phase is of first order. In $PyrAg_5I_6$, however, this transition takes place without a change of phase. At $-30^\circ C$ the Ag^+ ions in $PyrAg_5I_6$ are essentially ordered; the 10 Ag^+ ions per unit cell occupy the 4c and 6f sites of the hexagonal unit cell, belonging to the space group $P6/mcc$ (D_{6h}^2). With increasing temperature these sites are gradually depopulated and the Ag^+ ions partly occupy the 24m sites. Above about $50^\circ C$ the system is in a state of high disorder. Similar gradual order-disorder transitions have been observed in some anion conductors.⁴

In this paper we present specific-heat data of $PyrAg_5I_6$ and single-crystal conductivity measurements both along and perpendicular to the hexagonal axis. In a model calculation of the site occupancies and the specific-heat contribution from the disordering of the Ag^+ ions, using the quasi-chemical approximation, we account for the main features of the transition and investigate the role of correlations between the Ag^+ ions.

II. EXPERIMENTAL

Pyridinium iodide was obtained from pyridine (Merck, analytical) and hydrogen iodide (57%) (Merck, analytical) and was recrystallized several times from ethanol. Crystals of $PyrAg_5I_6$ were grown from hydrogen iodide (57%) by a con-

vection method. The growing solution was prepared by saturating the hydrogen iodide solution first with AgI (Merck) and afterwards with a 1:5 molar mixture of PyrI and AgI at $35^\circ C$. This solution was introduced into the crystal growing apparatus (Fig. 1) consisting of a compartment which was held at $40^\circ C$ (T_1), connected at the top and at the bottom to a compartment held at $30^\circ C$ (T_2). When necessary the velocity of circulation of the liquid was reduced by some glass wool. In the $40^\circ C$ compartment, powdered $PyrAg_5I_6$ was introduced in a glass container having some slits in the bottom. The crystals grew on the walls of the $30^\circ C$ compartment. After a few weeks the crystals were collected. Needles up to 5-mm long with a cross section of 1 mm were obtained in this way. Crystals of $Pyr_3Ag_{18}I_{23}$ were grown in a

FIG. 1. Crystal growing apparatus for $PyrAg_5I_6$.

similar way.

Satisfactory contacts for conductivity measurements were made by putting the crystals between spring-loaded amalgamated silver plates. Above about 100 Hz the real part of the impedance was almost constant and the imaginary part was very small. This is in contrast to painted or evaporated silver contacts, which showed more or less a Warburg behavior⁵ up to 100 kHz. The conductivity measurements were carried out either with a Wayne-Kerr bridge at 10 kHz or a Hewlett Packard 4800A vector impedance meter at 100 kHz.

The specific heat was measured with a Perkin Elmer model 2 differential scanning calorimeter. By comparing the measured and known specific heat of sapphire, the error in the specific-heat measurements was estimated to be less than 5%.

III. RESULTS

The specific heat of PyrAg_5I_6 shows two anomalies (Fig. 2). The small asymmetric peak at about 220 °K is indicative of a second-order phase transition. The low-temperature structure is monoclinic as ascertained from rotation x-ray photographs. The transition is probably a precursor to an ordering of the pyridinium ions, which are statistically distributed over six possible orientations in the hexagonal phase.² A more extensive account of the structural aspects of this phase transition will be given elsewhere.⁶

The Schottky-type anomaly with a maximum at 310 °K is associated with the disordering of the Ag^+ ions. The specific heat changes continuously over a relatively wide temperature range. The temperature at which the specific heat reaches its maximum is about ten degrees lower than the temperature defined by the change in slope of the conductivity and structural data of Geller and Owens²—

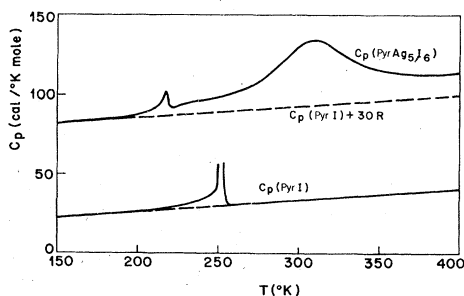


FIG. 2. Specific heat of PyrAg_5I_6 , showing the Schottky-type anomaly associated with the disordering of the Ag^+ ions and a second-order phase transition at about 220 °K. Also shown is the vibrational part of the specific heat, calculated from the measured specific heat of PyrI and the specific heat of AgI , which was taken to be $6R \text{ cal}^\circ\text{K}^{-1} \text{ mole}^{-1}$ over the temperature range involved.

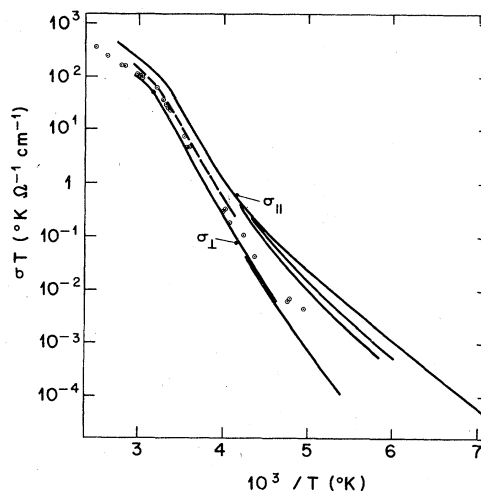


FIG. 3. Plot of the ionic conductivity of single crystals of PyrAg_5I_6 , parallel to the hexagonal axis (σ_{\parallel}) and perpendicular to it (σ_{\perp}). For comparison the powder measurements of Geller and Owens (Ref. 2) are shown too (circles). These data should be compared with the broken line, representing the corresponding values, calculated from our single-crystal data.

showing that the transition temperature is not well defined.

To compare the specific-heat contribution from the disordering process with the calculations in Sec. V, it is necessary to subtract the vibrational part of the specific heat, consisting not only of the contributions of the phonons, but also of the intramolecular vibrations of the pyridinium ions. Because we do not have all data necessary to calculate this contribution, we will assume that it is equal to the specific heat of the components. The specific heat of PyrI was measured, and is also shown in Fig. 2. The peak at 251 °K from a phase transition, was subtracted. The experimental specific heat of AgI itself is anomalous,⁷ and therefore we have approximated it by the classical value of $3kT$ per ion, which seems to be reasonable in the temperature range involved. At low temperatures the experimental curve and the one calculated from the constituents almost coincide, as is evident from Fig. 2. Therefore, it may be assumed that the above procedure also gives reasonable results at higher temperatures. The specific-heat contribution from the disordering of the Ag^+ ions obtained in this way is shown in Fig. 5 for five different samples. A correction to convert C_p to C_v was not applied.

In Fig. 3 the experimental ionic conductivity data have been summarized. At the phase transition of 220 °K only a very small discontinuity was observed for two out of three crystals. Below this temperature the results are somewhat dif-

TABLE I. Specific conductivity values at room temperature and low-temperature limiting activation energies of PyrAg_5I_6 , parallel and perpendicular to the hexagonal axis.

$\sigma_{\parallel}^{295^\circ\text{K}}$ ($\Omega^{-1}\text{cm}^{-1}$)	$\sigma_{\perp}^{295^\circ\text{K}}$ ($\Omega^{-1}\text{cm}^{-1}$)	E_{\parallel} (eV)	E_{\perp} (eV)
0.17	0.04	0.26	0.42

ferent for different crystals. The slopes of the curves at low temperatures, however, are almost the same. The low-temperature activation energies and the absolute values at room temperature are given in Table I. The absolute value of σ_{\perp} is somewhat uncertain, presumably because of the varying quality of the contacts with the amalgamated silver electrodes. The agreement between the powder measurements of Geller and Owens² and the corresponding values calculated from our data, using the relation

$$\sigma_p = \frac{1}{3}(\sigma_{\parallel} + 2\sigma_{\perp}), \quad (1)$$

is very good. In order to avoid the interference of σ_{\perp} and σ_{\parallel} , crystals used for the measurement of σ_{\parallel} were chosen to have an l/d ratio as large as possible,⁸ where l is the length of the hexagonal needle and d is the cross section. In practice an l/d ratio of five was realized, which allows one to measure anisotropy factors up to about 25.

In addition, the conductivity of the bright yellow crystals of $\text{Pyr}_5\text{Ag}_{18}\text{L}_{23}$ were measured in the same way. The measurements confirm the prediction of Geller *et al.*⁹ that this material is a two-dimensional conductor. At room temperature the value of σ_{\parallel} was found to be three to four orders of magnitude less than σ_{\perp} . For σ_{\perp} a value of $1.7 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$ was found. The real value for σ_{\perp} , however, must be higher because the l/d ratio of the crystals used was about one—far too large to avoid a mixing of σ_{\perp} and σ_{\parallel} . The activation energy for σ_{\perp} of 0.21 eV, obtained from measurements over the temperature range of 160–300 °K, is in perfect agreement with the value from powder measurements.⁹ No anomalous contribution to the specific heat was observed between 100 and 400 °K for this material.

Both the specific-heat data and the conductivity data of PyrAg_5I_6 suggest that interactions between the Ag^+ ions play an important role. The specific-heat anomaly is much sharper than would be expected on a model taking into account only the differences in site energy.¹⁰ The rather drastic increase of the slope of the $\log\sigma_{\parallel}$ vs $1/T$ curve at the low-temperature side of the transition even suggests that the excitation of Ag^+ ions to the m sites occurs to some extent in a cooperative way. Such

a behavior is expected if the interactions between the conducting ions are such that they tend to stabilize the ordered low-temperature state, but on the other hand allow for a disordered state at high temperatures. This will be the case if the interaction between ions on sites which are empty in the ordered state (the m sites in PyrAg_5I_6) and ions on sites being occupied in the ordered state (the c and f sites) is strong and repulsive. This is easily seen to be true for simultaneously occupied m and f sites,² because the distance between the sites is only 1.6 Å, but is less obvious for simultaneously occupied neighboring m and c sites.

The simplest approximate method to describe order-disorder phenomena, including correlation effects in an average way, is the Bragg-Williams approximation. This approach was used recently by Pardee and Mahan¹¹ in their theoretical treatment of the thermodynamics and transport properties of solid electrolytes. In contrast to these authors, we found that this approximation results in a rather poor fit of the experimental fractional occupancies of the Ag^+ ions in PyrAg_5I_6 .¹² At low temperature the calculated curves vary too smoothly with temperature, whereas at high temperature they approach the asymptotic high temperature value of $\frac{10}{34}$ too fast. In addition, a first-order phase transition is obtained for U/Δ ratios larger than 1.2.¹³ To improve on this we will use the quasichemical approximation, a method, taking short-range order into account more explicitly.

IV. QUASICHEMICAL APPROXIMATION

The quasichemical approximation of Fowler and Guggenheim¹⁴ has been successfully applied to describe order-disorder phenomena in binary alloy systems. It has the advantage over other methods of being applicable to more complex systems.¹⁵ Wiedersich and Johnston¹⁶ have used this method to calculate the excess specific heat from disorder of the Ag^+ ions in RbAg_4I_5 . The cluster variation method, which was applied to β -alumina by Kikuchi and Sato¹⁷ gives identical results to the quasichemical method up to the pair approximation.

Instead of applying the method directly to the PyrAg_5I_6 compound, it seems worthwhile to re-derive the general equations for a solid electrolyte. To this end, we consider a solid in which ions of only one kind are distributed over several different types of sites. Of the total number N_{α} of sites of type α , a fraction ρ_1^{α} is occupied and a fraction $\rho_0^{\alpha} = 1 - \rho_1^{\alpha}$ is empty. Interactions between the ions are taken into account up to the nearest neighbors. The total energy of the system as far as the conduction ions are concerned may be expressed as

$$E = \sum_{\alpha} \sum_{\beta \leq \alpha} \sum_{i,j} Q_{\alpha\beta} q_{ij}^{\alpha\beta} c_{ij}^{\alpha\beta}, \quad (2)$$

TABLE II. Relations between the quantities ρ_i^α and $q_{ij}^{\alpha\beta}$.

$q_{ij}^{\alpha\beta} = q_{ji}^{\beta\alpha}$	$\sum_i \sum_j q_{ij}^{\alpha\beta} = 1$
$\sum_i q_{ij}^{\alpha\beta} = \rho_j^\beta$	$\sum_i \rho_i^\alpha = 1$
$\sum_j q_{ij}^{\alpha\beta} = \rho_i^\alpha$	$Q_{\alpha\beta} = z_{\alpha\beta} N_\alpha = z_{\beta\alpha} N_\beta$

where the total number of neighboring pairs of α and β sites ($Q_{\alpha\beta}$) has been divided into four categories depending on whether the sites are occupied or empty. The index i takes on the value 1 if site α is occupied and the value 0 if site α is empty, and j does the same with respect to β . The $\epsilon_{ij}^{\alpha\beta}$ represent the energies of these pairs. The $q_{ij}^{\alpha\beta}$ are the fractional number of ij pairs and are mutually dependent quantities. Their relationships are given in Table II. Using these relations, Eq. (1) may be rewritten

$$E = E_0 + \sum_\alpha N_\alpha \rho_1^\alpha \epsilon_\alpha + \sum_\alpha \sum_{\beta \leq \alpha} Q_{\alpha\beta} q_{11}^{\alpha\beta} \epsilon_{\alpha\beta}, \quad (3)$$

with

$$E_0 = \sum_\alpha \sum_{\beta \leq \alpha} Q_{\alpha\beta} \epsilon_{00}^{\alpha\beta}, \quad (3a)$$

$$\epsilon_\alpha = \sum_\beta z_{\alpha\beta} (\epsilon_{10}^{\alpha\beta} - \epsilon_{00}^{\alpha\beta}), \quad (3b)$$

$$\epsilon_{\alpha\beta} = \epsilon_{11}^{\alpha\beta} + \epsilon_{00}^{\alpha\beta} - \epsilon_{10}^{\alpha\beta} - \epsilon_{01}^{\alpha\beta}. \quad (3c)$$

$z_{\alpha\beta}$ is the number of nearest-neighbor β -type sites of a site of type α . E_0 may be taken as the zero of energy. The second term of Eq. (3) is the sum of single-particle energies, and the last term contains the effective nearest-neighbor interaction energies.

Now, according to the quasichemical approximation the total number of possible configurations of ions is proportional to the number of ways one can divide the $Q_{\alpha\beta}$ pairs into the four groups of pairs defined above, i.e.,

$$W = K \prod_\alpha \prod_{\beta \leq \alpha} \left(\frac{Q_{\alpha\beta}!}{\prod_i \prod_j (Q_{\alpha\beta} q_{ij}^{\alpha\beta})!} \right). \quad (4)$$

K is a normalizing factor, which may be determined by noting that the values of the $q_{ij}^{\alpha\beta}$ which maximize W are the values $q_{ij}^{\alpha\beta} = \rho_i^\alpha \rho_j^\beta$, corresponding to complete randomness, so that

$$W^* = \prod_\alpha \left(\frac{N_\alpha!}{\prod_i (N_\alpha \rho_i^\alpha)!} \right). \quad (5)$$

Hence

$$W = \prod_\alpha \left(\frac{N_\alpha!}{\prod_i (N_\alpha \rho_i^\alpha)!} \right) \prod_\alpha \prod_{\beta \leq \alpha} \prod_i \prod_j \left(\frac{(Q_{\alpha\beta} \rho_i^\alpha \rho_j^\beta)!}{(Q_{\alpha\beta} q_{ij}^{\alpha\beta})!} \right). \quad (6)$$

The equilibrium configuration of the system is obtained by maximizing $\ln W$ with respect to the parameters ρ_i^α and $q_{11}^{\alpha\beta}$, subject to condition (3) and

$$\sum_\alpha N_\alpha \rho_1^\alpha = n, \quad (7)$$

where n is the total number of conduction ions in the system. This procedure results in a set of coupled equations

$$\ln \left(\frac{\rho_1^\alpha}{\rho_0^\alpha} \right) + \sum_\beta z_{\alpha\beta} \ln \left(\frac{\rho_0^\alpha q_{10}^{\alpha\beta}}{\rho_1^\alpha q_{00}^{\alpha\beta}} \right) = \frac{-(\epsilon_\alpha - \mu)}{kT}, \quad (8a)$$

$$\ln(q_{10}^{\alpha\beta} q_{01}^{\alpha\beta} / q_{11}^{\alpha\beta} q_{00}^{\alpha\beta}) = \epsilon_{\alpha\beta} / kT, \quad (8b)$$

where μ is the chemical potential.

From Eqs. (7) and (8) the temperature dependence of the fractional occupancies ρ_i^α and the fractional number of pairs of simultaneously occupied α and β sites $q_{11}^{\alpha\beta}$ can be determined if the energies ϵ_α and $\epsilon_{\alpha\beta}$ are known. The configurational entropy is given by

$$S = k \sum_\alpha \left[\left(\sum_{\beta \leq \alpha} Q_{\alpha\beta} - N_\alpha \right) \sum_i (\rho_i^\alpha \ln \rho_i^\alpha) + \sum_{\beta \leq \alpha} Q_{\alpha\beta} \sum_{ij} (q_{ij}^{\alpha\beta} \ln q_{ij}^{\alpha\beta}) \right] \quad (9)$$

and the specific heat may be calculated from

$$C_V = \sum_\alpha N_\alpha \epsilon_\alpha \left(\frac{\partial \rho_1^\alpha}{\partial T} \right)_V + \sum_\alpha \sum_{\beta \leq \alpha} Q_{\alpha\beta} \epsilon_{\alpha\beta} \left(\frac{\partial q_{11}^{\alpha\beta}}{\partial T} \right)_V. \quad (10)$$

V. APPLICATION TO PyrAg_5I_6

In PyrAg_5I_6 there are three types of sites over which the Ag^+ ions are distributed, i.e., $6f$, $4c$, and $24m$ sites.² Every c site has six m and two other c sites as nearest neighbors, every f site has four m sites as nearest neighbors, and every m site has one m , one f , and one c site as a nearest neighbor. Therefore, if we would apply the above equations as such to this material, we would have six unknown energy parameters; i.e., $\epsilon_m - \epsilon_c$, $\epsilon_f - \epsilon_c$, ϵ_{cc} , ϵ_{cm} , ϵ_{fm} , and ϵ_{mm} . One way to simplify the problem is to assume some kind of relation between the interaction energies. In applying the quasichemical approximation to the solid electrolyte RbAg_4I_5 , Wiedersich and Johnston¹⁶ assumed that the interaction energies are inversely proportional to the interionic distances. However, such a simple relation is not realistic, in particular because these interaction energies also contain contributions caused by deformation of the iodide framework. Even if these parameters were known, the method is expected to give only qualitative agreement because of the neglect of high-order clusters. Therefore, we will try to reproduce the

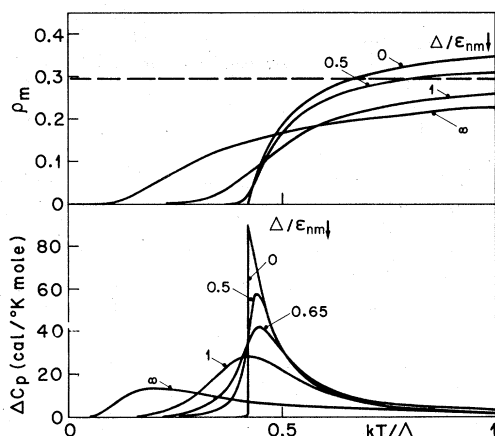


FIG. 4. Calculated site occupancy and specific heat for a two-site system in the quasichemical approximation. Two parameters of the model are the site energy difference Δ and the nearest-neighbor pair interaction energy ϵ_{nm} .

main features of the transition by taking into account only the most important of the above parameters.

The terms containing the interaction between ions on like sites are not expected to contribute much to the free energy of the system. Although ϵ_{nm} may be quite large because the distance between neighboring m sites is only 2.0 \AA ,² the number of pairs of simultaneously occupied neighboring m sites will be very small anyway, because the fractional occupation of m sites is small over the whole experimental temperature range. Consequently, both the energy and entropy contributions to the free energy from these pairs will be small. A similar argument, though less rigorous, may be used to justify the neglect of interactions between neighboring empty c sites. As we have already argued in Sec. IV, the interactions between ions on c or f sites and on m sites are expected to be important. We will now make the apparently very crude assumption that the c and f sites can be considered as identical as far as the site energies and the interaction energies are concerned. The basis for this assumption is that the experimental site occupancies of the c and f sites are equal within the experimental limits of error over the temperature range involved.² In this way we have reduced the problem to a two-site system. The sites which are occupied in the ordered state will be referred to as n sites, and the empty sites will be referred to as m sites. The number of nearest-neighbor m sites was taken to be 4.8 so that the relation $z_{nm}N_n = z_{mn}N_m$ is still valid.

For a two-site system having g times as many m as n sites Eq. (8) reduce to

$$\ln\left(\frac{1-g\rho}{g\rho}\right) + z_{nm} \ln\left(\frac{g\rho(1-g\rho-q)}{(1-g\rho)(g\rho-\rho+q)}\right) \\ = \ln\left(\frac{\rho}{1-\rho}\right) + z_{mn} \ln\left(\frac{(1-\rho)(\rho-q)}{\rho(g\rho-\rho+q)}\right) + \frac{\Delta}{kT} \quad (11a)$$

and

$$\ln[(1-g\rho-q)(\rho-q)/q(g\rho-\rho+q)] = \epsilon_{nm}/kT. \quad (11b)$$

ρ is the fractional occupancy of m sites, q is the number of pairs of simultaneously occupied n and m sites, and Δ is the site energy difference between m and n sites. In obtaining Eq. (11) we have introduced

$$\rho_1^n = 1 - g\rho_1^m = 1 - g\rho, \quad (12)$$

which follows from Eq. (7).

Putting $g=2.4$, $z_{nm}=4.8$, and $z_{mn}=2$, we have calculated ρ and C_V numerically as a function of kT/Δ for different ratios of Δ/ϵ_{nm} . The results of this calculation are shown in Fig. 4.

At low temperatures, Eq. (11) yield a simple expression for ρ and q

$$\rho = q = g^{-1/2} \exp[-(\Delta + z_{mn}\epsilon_{nm})/2kT]. \quad (13)$$

This exponential increase of ρ is easily understood. At low temperatures the deviation from the ordered state is very small and almost every ion at an m site has z_{mn} neighbors, adding an amount $z_{mn}\epsilon_{nm}$ to the energy necessary to create a Frenkel pair. As the disorder increases, excitation of ions to m sites becomes easier because the probability that the ions occur in configurations such that the interactions between them are small increases at higher temperatures, and ρ increases more rapidly with temperature than according to Eq. (13). This is most clearly demonstrated for the case that ϵ_{nm} is very large with respect to Δ . Initially ρ is essentially zero because the creation of single Frenkel pairs is not possible. Above $T = 0.42\Delta/k$ the entropy contribution to the free energy of more complicated clusters of ions exceeds the energy contribution and the disordering process suddenly starts. At very high temperatures ρ approaches the value $1/(g+1) = 0.294$ as it should for complete randomness.

From Fig. 4 it is seen that for ϵ_{nm}/Δ ratios larger than one, the position of the maximum in the specific heat is mainly determined by the site energy difference Δ ; whereas the interaction parameter ϵ_{nm} is responsible for the shape of the curve at the low-temperature side of the transition. It should be noted that for all positive values of the ratio Δ/ϵ_{nm} Eq. (11) only have one solution and that no first- or second-order phase transition occurs, in agreement with the experimental result that the space group and unit cell content do not change through the transition.²

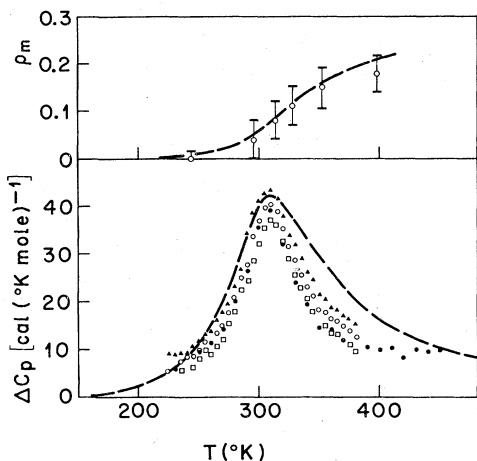


FIG. 5. Best fit of the model calculation to the experimental site occupancy of the m sites of Geller and Owens (Ref. 2) and the excess specific heat. For the site energy difference Δ a value of 0.065 eV and for the interaction energy parameter ϵ_{nm} a value of 0.092 eV was used.

VI. DISCUSSION

The best fit to both the experimental fractional occupation of m sites taken from Ref. 2 and our specific-heat data is shown in Fig. 5. In view of the approximations involved, the theoretical curves are seen to reproduce the experimental data surprisingly well. This fit was obtained for a value of 0.065 eV for the site energy difference Δ , and 0.092 eV for the interaction energy ϵ_{nm} .

The value of the latter parameter is large with respect to kT , even at temperatures above the transition. This means that a simultaneous occupation of neighboring m and c sites as well as m and f sites is very unlikely over the whole experimental temperature range. Instead, the ions prefer to form configurations in which nearest-neighbor contact can be avoided. With increasing disorder, the probability to excite an ion from a c or f site to an m site, subject to the above restriction, increases rapidly. This is the reason that the site occupancy, the conductivity, and the specific heat initially increase more than exponentially with temperature.

The strong repulsions between the ions also lead to a more nonrandom distribution of ions in the disordered state above the transition. If the ions were uniformly distributed over the available sites, all site occupancies would be equal and have the value 0.294. From our calculation we obtain a value of 0.21 at 125 °C, which is in reasonable agreement with the experimental value of 0.18 ± 0.04 .²

As we have already shown in Sec. V, at sufficiently low temperatures the model predicts that

Frenkel pairs will take over from more complicated clusters of ions. The conductivity at low temperatures may be considered to result from two kinds of independent charge carriers: the ions at m sites and the vacancies at c and f sites. Within the limitations of the model, their number is given by Eq. (13). As proposed by Geller,¹⁸ we will assume that the ions move through faces shared by the anion polyhedra. The network of possible passageways is schematically drawn in Fig. 6. While there are no paths connecting only the m sites throughout the whole crystal, an ion at an m site can only move via vacant c or f sites. Because almost all these sites are occupied at low temperatures, the probability for this to happen is extremely small. At these temperatures the ions at m sites are therefore not expected to contribute much to the dc conductivity. For the vacancies on the other hand, there are several possibilities to move from one site to another.

The pathways giving the conductivity perpendicular to the c axis always must involve m sites (c - m - f). The potential barrier between c (or f) and m sites thus determines the activation energy of the conductivity in that direction.

The motion of the ions along the c axis may also proceed via m sites (c - m - m - c , c - m - m - f , f - m - m - f). The potential barriers for these jump processes are likely to be of the same order of magnitude or even in excess of the potential barrier in the process governing the conductivity perpendicular to the c axis. In addition to the fact that the same types of jumps are involved, the ion must pass by an occupied c or f site. From the experimental low-temperature activation energies for the conductivity (see Table I), however, it may be deduced that the barrier for the motion of the Ag^+

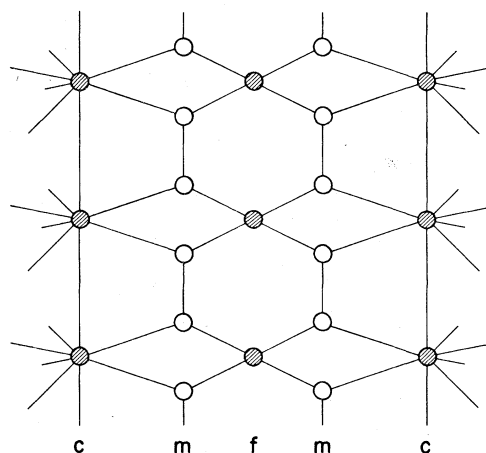


FIG. 6. Schematic drawing of the possible passageways for conduction of the Ag^+ ions in PyrAg_5I_6 .

ions along the c axis is considerably smaller. This suggests that the conductivity along the c axis results primarily from vacancies of c sites moving directly to neighboring c sites.

A rough estimate of the potential barriers, using the experimental activation energies for the conductivity and assuming that the number of Frenkel pairs is correctly predicted by Eq. (13) with $\Delta = 0.065$ eV and $\epsilon_{mm} = 0.092$ eV, gives a value of about 0.1 eV for the barrier between neighboring c sites and 0.3 eV for the barrier between c or f sites and m sites.

The above considerations confirm^{2,19} that the conductivity in PyrAg_5I_6 predominantly proceeds via the channels provided by the c sites.

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¹S. Geller, *Science* **176**, 1016 (1972).

²S. Geller and B. B. Owens, *J. Phys. Chem. Solids* **33**, 1241 (1972).

³See, for example, B. B. Owens, in *Advances in Electrochemistry and Electrochemical Engineering*, edited by C. U. Tobias (Wiley, New York, 1971), Vol. 8, pp. 1-61; *J. Electrochem. Soc.* **117**, 1536 (1970); B. B. Owens, J. H. Christie, and G. T. Tiedeman, *ibid.* **118**, 1144 (1971); *Inorganic Chem.* **14**, 1423 (1975); T. Takahashi, S. Ikeda, and O. Yamamoto, *J. Electrochem. Soc. Jpn.* **120**, 647 (1973); **119**, 477 (1972).

⁴A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* **72**, 1277 (1968); M. O'Keefe, in *Fast Ion Transport in Solids*, edited by W. van Gool (North-Holland, Amsterdam, 1973).

⁵J. R. MacDonald, *J. Electroanal. Chem. Interfacial Electrochem.* **47**, 182 (1973).

⁶T. Hibma and S. Geller, *J. Solid State Chem.* (to be published).

⁷S. Pitzer, *J. Amer. Chem. Soc.* **63**, 516 (1941); K. H. Lieser, *Fortsch. Mineralog.* **36**, 96 (1958).

⁸H. R. Zeller and A. Beck, *J. Phys. Chem. Solids* **35**, 77 (1974).

⁹S. Geller and P. M. Skarstad, *Phys. Rev. Lett.* **33**, 1484 (1974); S. Geller, P. M. Skarstad, and S. A. Wilber, *J. Electrochem. Soc.* **122**, 332 (1975).

¹⁰H. Wiedersich and S. Geller, in *The Chemistry of Extended Defects in Non-metallic Solids*, edited by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, 1969).

¹¹W. J. Pardee and G. D. Mahan, *J. Solid State Chem.* **15**, 310 (1975).

¹²In a private communication the authors of Ref. 11 acknowledge that their calculation of the site occupancies in PyrAg_5I_6 contains a numerical error, leading to an asymptotic high-temperature value of 0.21 for p sites and 0.5 for n sites (Fig. 6 of Ref. 11), instead of $\frac{10}{34}$ for both kinds of sites.

¹³L. Pietronero and S. Strässler (unpublished).

¹⁴R. H. Fowler and E. A. Guggenheim, *Proc. R. Soc. Lond. A* **174**, 189 (1940); *Statistical Mechanics*, (Cambridge U.P., Cambridge, 1960).

¹⁵T. Muto and Y. Takagi, *Solid State Phys.* **1**, 193 (1955).

¹⁶H. Wiedersich and W. V. Johnston, *J. Phys. Chem. Solids* **30**, 475 (1969).

¹⁷H. Sato and R. Kikuchi, *J. Chem. Phys.* **55**, 677 (1971); **55**, 702 (1971).

¹⁸S. Geller, in *Fast Ion Transport in Solids*, edited W. van Gool (North-Holland, Amsterdam, 1973).

¹⁹S. Geller, in *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976).