[3] The data refer to perdeuterated species, but the isotopic differences are expected to be smaller than the experimental errors and are neglected.

[4] J. A. Pople and G. A. Segal, J. Chem. Phys. 43, S136 (1965); 44, 3289 (1966).

[5] J. A. Pople and M. Gordon, J. Am. Chem. Soc. 89, 4253 (1967).

[6] See, S. Ehrenson, J. Am. Chem. Soc. 91, 3702 (1969).

[7] See Ref. 1 for a review of calculations on H_3O^+ culminating in the apparently definitive *ab initio* LCAO MO Gaussian orbital study of Hopkinson *et al.* (Ref. 8).

[8] A. C. Hopkinson, N. K. Holbrook, K. Yates, and I. G. Csizmadia, J. Chem. Phys. 49, 3596 (1968). The only calculation on higher solvated species of the proton is due to Grahn (Ref. 9), who applied a valence-bond treatment to the structure of $H_9O_4^+$ shown in Fig. 4.

[9] R. Grahn, Arkiv Fysik 21, 13 (1961).

[10] E. Wicke, M. Eigen, and Th. Ackermann, Z. Physik. Chem (Frankfurt) 1, 340 (1954).

[11] P. A. Kollman and L. C. Allen, J. Chem. Phys. 51, 3286 (1969).

[12] S. Ehrenson and S. Seltzer (unpublished).

[13] R. R. Bernecker and F. A. Long, J. Phys. Chem. 65, 1565 (1961).

[14] F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957).

[15] From the studies of Pople and Gordon,[5] where the nominally less ionic bonding in substituted hydrocarbons was examined but where substantial charge alternation was observed, one is led to conclude that perhaps part of the severe pileup of charge on bridge oxygens is a reflection of method and hence that the charges should only be judged in the context of similarly examined molecules. The excellent dipole moments obtained in Ref. 5, of course, suggest these charges may be real. At any rate, the qualitative trends as regards shielding of strongly positive bridging protons by intermediate chain oxygens must be judged as entirely reasonable.

[16] See J. O'M. Bockris and B. E. Conway, *Modern Aspects of Electrochemistry* (Butterworths Scientific Publications, Ltd., London, 1964).

Heat Capacity of Silver Iodide. IV. Heat Content of Quenched Stoichiometric Material

C. M. Perrott* and N. H. Fletcher

Department of Physics, University of New England, Armidale N.S.W., Australia

(Received 29 September 1969)

Experiments have been performed to measure the heat content of stoichiometric silver iodide, water quenched from the high-temperature (α) phase to room temperature. The data shows the retention of large amounts of energy during quenching, and this is shown to be consistent with a model of lattice disorder which was developed to explain anomalous thermal properties of annealed material.

I. INTRODUCTION

In the first three papers of this series,[1,2,3] we have presented experimental data which shows that the heat capacity of annealed stoichiometric α-AgI is truly anomalous. This phase of silver iodide, stable between 150°C and the melting point 555°C, has a heat capacity which increases progressively with increasing temperature before a sudden fall to a near-normal value for temperatures above 430°C (Fig. 1). The sudden change in heat capacity at 430°C is associated with a latent heat which cannot be attributed to any known phase transformation in the material.

This unusual behavior is befitting the unusual structure of the material. According to the structural model proposed by Strock[4] and later verified by Hoshino,[5] the anions occupy the sites of a regular bcc lattice while the cations are distributed more or less randomly throughout the spaces of this lattice. Strock proposed that the two silver ions in the unit cell are distributed with equal probability over a total of 42 sites (Fig. 2), but Hoshino showed that the data, being obtained by x-ray powder diffraction studies, cannot give unequivocal evidence concerning the statistics of this distribution.

We maintain that it is unreasonable to assume that the cations are distributed on an independent-particle basis, but rather, correlations between the positioning of these ions must be included in any reasonable model of the material. The extent of these correlations or the degree of cation order will necessarily decrease with increasing temperature, and like all cooperative phenomena, this disordering should give rise to anomalous thermal properties.

In fact, the curve shown in Fig. 1 is typical of the heat capacity curves obtained with alloys which undergo order–disorder transitions. The Strock model being incapable of explaining this behavior, we have justified our reconsidered model of the cation distribution by showing that the behavior is consistent with the proposition that the cations disorder progressively with increasing temperature until the critical temperature, 430°C, where the disordering is suddenly completed.

A simple formulation of these ideas in terms of three bcc sublattices, which can be used to specify the cationic distribution, has been described and gives good agreement with experiment when the mathematical simplifications are remembered. In order to check the physical ideas of our model, rather than the mathematical details, we have performed heat content experiments on stoichiometric samples. The data obtained is very complicated and sensitive to the prior treatment of

samples and will be seen to support our model rather than that of Strock.

In order to limit the discussion, we will treat the detailed results obtained with samples which have been water quenched and mention other results only where they are pertinent. In all cases, the data will be characterized by plotting curves of δC_p, the amount by which the heat capacity is *increased* as a result of the quench.

II. EXPERIMENTAL RESULTS: QUENCHING

A. Results Obtained on Initial Reheating

The samples used for the experiments on annealed material were sealed into stainless-steel containers as described previously and then placed in a furnace and held at some desired temperature for a set time before being water quenched to room temperature. The heat
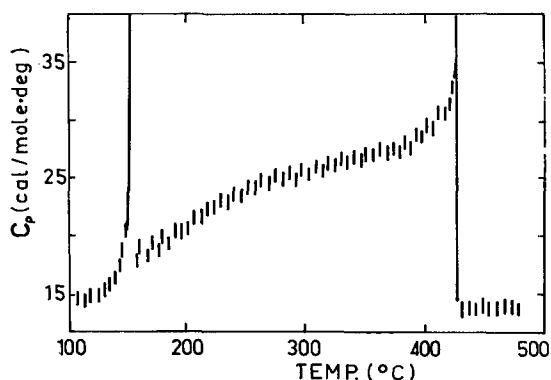
FIG. 1. Molar heat capacity of annealed samples of stoichiometric silver iodide. The graph points show the total scatter of values obtained with different samples on different heating runs.

capacity deviation δC_p, measured on reheating the samples, was typically of the form shown as Curve a in Fig. 3, when quenching was from some temperature *above* the β-to-α phase transformation at 150°C in silver iodide. No nonequilibrium effects were observed for quenches from below this temperature.

The behavior of samples quenched from the α phase is obviously complicated and involves a number of simultaneously occurring relaxation processes which we must separate before an analysis of the data is possible. When a sample was cooled rapidly (above 10 deg/min) in the calorimeter from some high temperature to one just above the 150°C phase transformation, the δC_p curve obtained on immediate reheating did not show any energy absorption effects near 150°C but showed the same high-temperature behavior as observed after quenching (Curve b, Fig. 3). This surely means that the energy absorption effect which we have labeled I is caused by the rapid cooling through the phase change rather than the rapid cooling of the disordered α phase. The other processes, however, would be expected for a
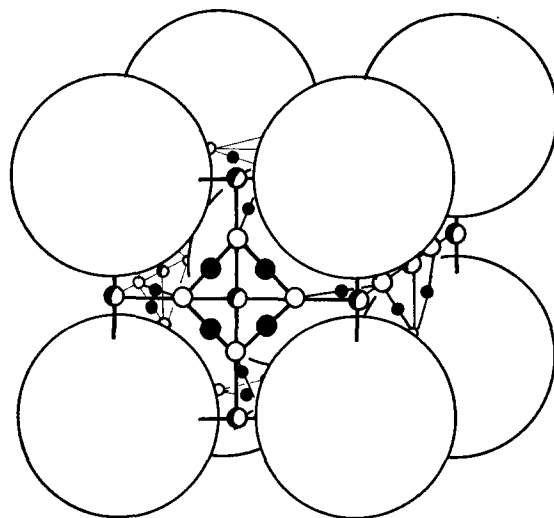
FIG. 2. Schematic drawing of the structure of α-AgI. The large spheres represent iodide ions and the remaining sites are available to silver ions.

hypothetical quench to 160° (say) and must therefore result entirely from the cooling of the α phase itself.

Examining these high-temperature phenomena in more detail, we found that the δC_p behavior for a particular quenching temperature was unaltered when the heating rate (during measurement) was doubled, except that the sharp peak labeled II shifted to a temperature approximately 30°C higher than before. In
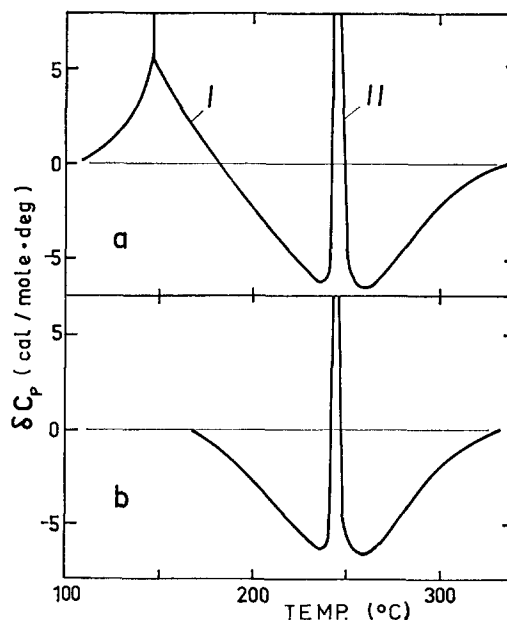
FIG. 3. Heat capacity deviation in stoichiometric AgI: (a) Initial heating of sample water-quenched from 350°C. Note the absorption processes (I and II) and the energy evolution (shown by negative values of δC_p). (b) Reheating immediately after cooling from 350 to 180°C at a rate of 10 deg/min.
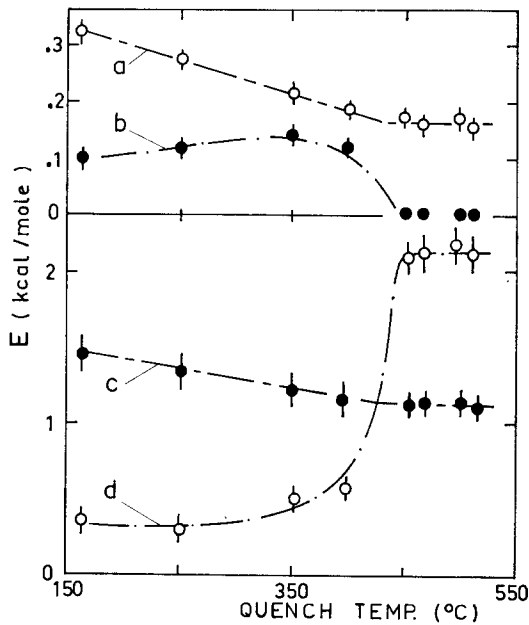
FIG. 4. Energy associated with nonequilibrium effects in water-quenched stoichiometric AgI: (a) absorption process II; (b) absorption process I; (c) latent heat of transformation at 150°C; (d) energy evolution process.

view of this, we believe that the high-temperature behavior of δC_p represents two nonequilibrium processes, one causing the dominant evolution of energy ($\delta C_p < 0$) and the other causing the sharp absorption spike II superimposed on the energy evolution profile.

The energy associated with each of these three non-equilibrium effects shown by the δC_p curves depends on quenching temperature. This dependence, together with that of the latent heat of transformation β to α-AgI, is shown in Fig. 4.
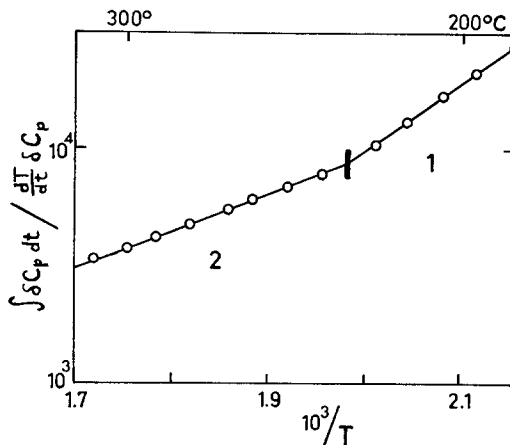

FIG. 5. Logarithmic plot which shows that the energy evolution process in quenched stoichiometric AgI occurs by relaxation under two monomolecular processes (for a quenching temperature of 450°C).

B. Discussion of the High–Temperature Behavior

Since we have seen that the high-temperature effects following water quenching of silver iodide are exactly those which would occur for a quench to 160°C, we can simplify the discussion by considering the data in terms of these hypothetical experiments which would involve only the α phase of the material. The relaxation of quenched-in defects causing the observed δC_p behavior can then be discussed in terms of the structure of α-AgI and its variation with temperature.

The dominant feature of the results is an extensive evolution of energy, the total energy release under the process being greater for higher quenching temperatures
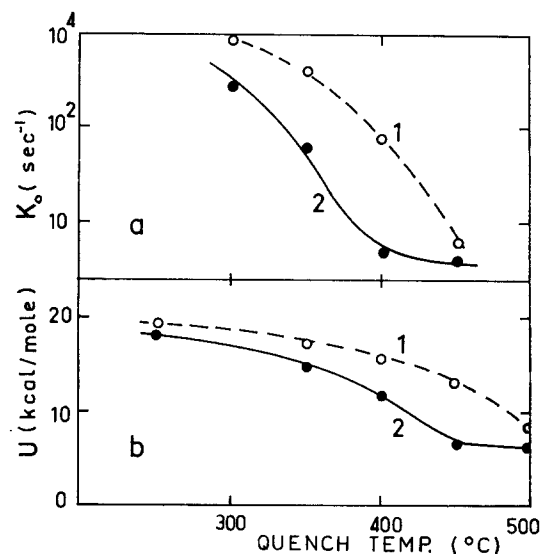

FIG. 6. Variation of (a) characteristic relaxation rates and (b) activation energies of the two relaxation processes associated with the energy evolution by quenched stoichiometric AgI.

(Curve d, Fig. 4). Logarithmic plots like that in Fig. 5 show that the release of the defect energy retained on quenching can be characterized by the equation

$$dE^D/dt = -[K_{0,1}\exp(-U_1/kT) + K_{0,2}\exp(-U_2/kT)]E^D,$$

which specifies relaxation of structural defects under two monomolecular processes involving diffusion to a set of sinks (e.g., surfaces) whose concentration and capture cross section remain independent of time. The characteristic relaxation rates ($K_{0,1}$ and $K_{0,2}$) and the activation energies (U_1 and U_2) of the two processes depend on the temperature from which the sample was quenched, as shown in Fig. 6.

This behavior is typical of that observed in similar experiments on alloys and could be attributed to the annealing of quenched-in vacancies, interstitials, or structural disorder. Adopting, for the moment, the Strock model of α-AgI, we see that the structural dis-

order is temperature independent, and its retention as a result of quenching cannot give rise to the observed effects. The only defects allowed by the model are vacancies and interstitials in the iodide lattice. Now, the activation energy Q for production of these defects in α-AgI is about 16 kcal/mole, and using the values of the activation energy for motion U (Fig. 6), we find that the energy of formation,

$$E = 2(Q-U),$$

is in the range 0–16 kcal/mole. Since the total energy release during annealing of these defects can be as high as 3 kcal/mole, an explanation based on the Strock model therefore requires defect concentrations in the iodide lattice of greater than 20%. This is clearly unreasonable and demonstrates the inadequacy of the Strock model of α-AgI.

Considering the data on the basis of our modified version of the Strock model, however, we find that the most likely type of defect encountered will be excessive cation disorder which can be retained even for very slow quenches. Since we have attributed the anomalous heat capacity of annealed material to the configurational disordering of cations, we may expect the energy release from quenched samples to be comparable with the integral of the anomalous heat capacity contribution between the quenching temperature and some temperature in the vicinity of 160°C. This is, in fact, the case, as can be seen from a comparison of Figs. 1 and 4(d). Furthermore, the magnitude of the energy release is seen to be unchanged for quenching temperatures above 430°C, as required by the existence of the critical temperature for disordering at that temperature.

Since our theoretical calculation gave reasonable agreement with the observed heat capacity of annealed samples, it must, on this model, also give at least semi-quantitative agreement with the quenching results. In addition, however, it implies that the relaxation of domains containing excessive cation disorder must be initiated by movement of the iodide ions which provide the physical interactions causing the cation ordering. That is, the activation energy for relaxation should be comparable to the activation energy for iodine self-diffusion[6] in α-AgI, 15 kcal/mole. Although the activation energies actually range from 8 to 20 kcal/mole (Fig. 6), this explanation must be appropriate because if silver ion movement initiated the relaxation, the activation energies[7] would be typically 1 kcal/mole. The variation of activation energies with quenching temperature could indicate the presence of a driving force whose magnitude increases as the severity of the quench increases.

We do not have sufficient evidence to allow identification of the mechanism leading to iodide ion motion, but a few observations can be made. If each ion were able to move independently, we should expect a relaxation
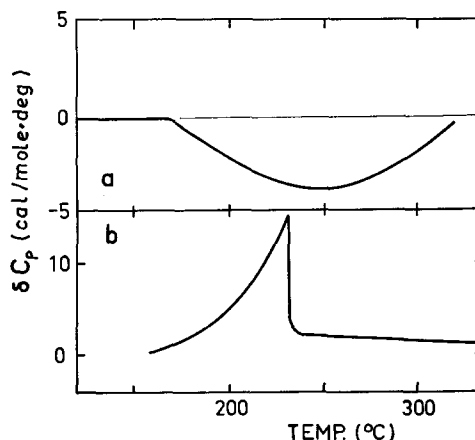

FIG. 7. Heat capacity deviation in stoichiometric AgI: (a) Compacted at room temperature in order to produce γ-AgI; (b) immediate reheating after cooling 300 to 160°C at 1 deg/min.

rate constant K_0 of the order of an atomic vibration frequency, 10^{13} sec^{-1}, rather than the observed value of 10–10^4 sec^{-1}. Better agreement is obtained if it is assumed that relaxation can only take place in the vicinity of itinerant iodide ion vacancies or mobile dislocations, being blocked in their absence by mechanical coupling between neighboring ions. This is, however, only speculation at present.

Despite the fact that the relaxation mechanism cannot yet be elucidated in detail, the very existence of the energy evolution process can be regarded as further justification of our partially ordered modification of the Strock model for the α-AgI structure.

It has been said that after quenching to room temperature,[8] silver iodide consists of a mixture of the phases β and γ AgI. Since our so-called "equilibrium" behavior is that of material which is entirely in the β form at room temperature, it is possible that some of the nonequilibrium behavior of quenched samples might be attributed to the presence of the γ phase. In order to check this possibility, samples of γ-AgI were prepared[8] by compaction at room temperature under a pressure greater than 100 bar and their heat capacity was measured on initial heating.

The results (Curve a in Fig. 7) show that the energy evolution process is associated with the presence of γ-AgI in the room temperature sample. This means that the domains of γ-AgI transform to domains of α-AgI which contain more cation disorder than the usual form of α-AgI derived from β-AgI. This deduction is consistent with x-ray powder diffraction data of Burley,[9] which showed that β and γ AgI do transform to slightly different forms of α-AgI, the difference occurring through the cation statistics.

Unlike the energy evolution process, the sharp absorption process II, observed near 250°C, has no obvious explanation. It has neither the form required for a monomolecular process nor the sign associated

with the usual defects encountered in single-phase systems. Rather, it has the essential features of a phase transformation with diffusion-controlled kinetics (c.f. the transition[10] from metastable ice I_c to ice I_h near $-80°C$). Although we might be tempted to attribute this to a transition between the two known forms of α-AgI, the data shows such an explanation to be untenable and we must be content to leave the effect unexplained.

C. Discussion of the Low-Temperature Results

The nonequilibrium effects observed as the energy absorption I and the depression of latent heat must be caused by the rapid traversal of the α to $(\beta+\gamma)$ AgI phase transformation. The effects are not observed with samples of γ-AgI prepared at room temperature and therefore have no explanation in terms of the existence of this phase in quenched material. Their exact origin cannot be deduced from the present data alone.

D. General Observations

Whatever their cause, the nonequilibrium effects observed must in some way reflect the equilibrium state of the material at the quenching temperature. The variation of their magnitudes with quenching temperature therefore indicates the variation of this equilibrium state. All curves of Fig. 4 show a steady temperature dependence which is interrupted near 430°C, above which no change occurs. It was exactly this observation which allowed the prediction of the 430°C anomaly[2] (Paper II of this series) which was later observed directly[3] (Paper III) and attributed to the occurrence of a critical temperature for disordering. If any other explanation had been appropriate, the curves of Fig. 4 should not have been continuous at 430°C and new processes should have entered for quenches from above this temperature.

III. OTHER HEAT CONTENT RESULTS

A. Rapid Cooling Experiments

A set of experiments was performed in which an annealed sample was cooled to 160°C and its heat capacity measured on reheating. The δC_p curves obtained for cooling rates faster than $\sim$10 deg/min were the same as that shown in Fig. 3(b) except that the energy release decreased in magnitude as the cooling rate was lowered. The absorption peak II showed no change until, for rather slow cooling rates ($\sim$4 deg/min), it split into two smaller peaks equally spaced about the position of the original peak. Partial annealing at 160°C before reheating resulted in a marked decrease in the separation of the two peaks. As the cooling rate was further decreased, the evolution process and the higher-temperature absorption peak disappeared, and for $\sim$1 deg/min cooling, the δC_p curves showed a single absorption peak [Fig. 7(b)].

B. Expansion Coefficient Anomaly

In the first paper of this series, we noted that the coefficient of thermal expansion calculated from the lattice parameter measurements of Hoshino[5] showed irregular fluctuations not indicated by the results of other workers. In fact, the C_p-C_v correction curve calculated on the basis of Hoshino's data shows a very sharp peak. This was ignored when we applied the correction to annealed material, but if we arbitrarily apply this anomalous correction to the heat capacity curve obtained after cooling the sample at 1 deg/min, we find that the C_v curve obtained is identical to that previously found for annealed samples.

This is coincidental, but is sufficient to show that Hoshino's anomalous results were probably caused by the prior treatment of the samples and indicates that absorption peak II, which we have not been able to explain, is possibly associated with a sudden expansion of the iodide lattice.

IV. CONCLUSION

The results presented in this paper are very complicated and a simple explanation of all of the detail is not obvious. Rather than attempt to deduce the complete picture, we have gone only as far with the analysis as required to show that when we modified the original Strock model of the material in an attempt to explain the results for annealed stoichiometric α-AgI, we did introduce the correct physical features, although our mathematical treatment was necessarily oversimplified.

* Present address: Division of Pure Physics, National Research Council of Canada, Ottawa, Canada.

[1] C. M. Perrott and N. H. Fletcher, J. Chem. Phys. **48**, 2143 (1968).
[2] C. M. Perrott and N. H. Fletcher, J. Chem. Phys. **48**, 2681 (1968).
[3] C. M. Perrott and N. H. Fletcher, J. Chem. Phys. **50**, 2770 (1969).
[4] L. W. Strock, Z. Physik. Chem. **B25**, 441 (1934); **B31**, 132 (1936).
[5] S. Hoshino, J. Phys. Soc. Japan **12**, 315 (1957).
[6] W. Jost and J. Nolting, Z. Physik. Chem. (Frankfurt) **7**, 383 (1956).
[7] K. H. Lieser, Z. Physik. Chem. (Frankfurt) **2**, 238 (1954).
[8] G. Burley, Am. Mineralogist **48**, 1266 (1963).
[9] G. Burley, Acta Cryst. **23**, 1 (1967).
[10] L. G. Dowell and A. P. Rinfret, Nature **188**, 1144 (1960).