species, in the case of the minor species. Thus, theory predicts resonance frequencies very close to the single-particle ion cyclotron frequencies and this is verified experimentally.

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†Permanent address: University of California, Los Angeles, Calif. 90024.

‡Permanent address: California Institute of Technology, Pasadena, Calif. 91109.

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# Ionic Conductivity near an Order-Disorder Transition: RbAg$_4$I$_5$†

R. Vargas,* M. B. Salamon, and C. P. Flynn
*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

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We report the first precise study of atomic mobility through a second-order phase transition. Simultaneous measurement of the ionic conductivity $\sigma$ and the specific heat near the 208-K transition of RbAg$_4$I$_5$ establishes an accurate proportionality between ln$\sigma$ and the ordering enthalpy $h$. This is interpreted using a many-body theory which treats local order beyond the mean-field approximation and in which the constant of proportionality is determined by microscopic details of the interaction among the mobile defects.

The mobile interstitials in some solids can diffuse with relative freedom among partially occupied sites connected by jump paths. In certain cases, the interactions among these mobile ions cause them to adopt partially ordered structures as the temperature is lowered.[1,2] Most treatments of the effect of ordering on the ionic mobility employ mean-field models which ignore important critical-point effects, and therefore predict that the activation energy should be unaffected by the phase transition above $T_c$ and should follow the square of the long-range order parameter below.[3] An exception to this approach is Mahan's attempt[4] to treat a lattice-gas model rigorously. However, no accurate prediction for the ionic mobility near the phase transition was obtained. In this Letter we present the first experimental determination of atomic mobility near a phase transition sufficiently accurate[5,6] to examine the *critical* behavior, and the first theoretical analysis to go beyond the mean-field approximation.[3,7] We establish, both experimentally and theoretically, that an accurate proportionality exists between the logarithm of the ionic conductivity, ln$\sigma$, and the interaction enthalpy, $h$, of the mobile-ion subsystem. This demonstrates the dominance of short-range order effects which have generally been ignored, and, through the constant of proportionality, gives microscopic information about the way short-range order modifies the energetics of the diffusive jump. The solid electrolyte RbAg$_4$I$_5$ has been employed because its conductivity provides a simple measure of mobility and because its 208-K phase transition has been shown to be Ising-like.[8]

The specific heat and the derivative $dR/dT$ of the resistivity of RbAg$_4$I$_5$ single crystals were measured simultaneously as functions of temperature using the ac method.[9] Crystals were grown in our laboratories using the solution technique with high-purity reagents.[10] Small single crystals were chosen as representative specimens for crystallographic identification. Buerger precession patterns showed quite uniform alignment and a cubic unit cell with a lattice constant of 11.24 Å, in good agreement with previous determinations.[11] Chemical analysis yielded a Ag-Rb atomic ratio of 4.2± 0.2.

Crystal slices were thinned to 0.1 mm using dry abrasives and connected to silver wires for four-terminal resistance measurements. 50-μm silver wires, coated with Ag paint, were heated in contact with the sample by passage of an electrical current. The diffused contacts produced in this way gave the smallest observed contact resistance. A constant ac current (12 μA at 10 kHz) was passed through the samples while they were heated by light chopped at 1.5 Hz. This induced temperature oscillations, inversely proportional to the specific heat, which were monitored using a 25-μm type-K thermocouple. The resulting amplitude modulation of the ac voltage was demodulated from the carrier and detected. From the temperature and voltage oscillations the specific heat $C_p$ and $dR/dT$ were obtained simultaneously as the temperature was varied slowing through the region of the phase transition.

Figure 1 shows the resistance $R(T)$ obtained by integrating $dR/dT$ through the critical region. For each sample, values obtained in this way agree with dc determinations of $R$ obtained at several temperatures. From $dR/dT$ and $R(T)$ we can calculate the logarithmic derivative $d(\ln\sigma)/dT$ shown in Fig. 2. This quantity exhibits critical behavior similar to that of the specific heat, which is also shown in Fig. 2.[8]

If the conductivity of $RbAg_4I_5$ is assumed to take the Arrhenius form

$$\sigma = (A/k_B T)\exp[-U(T)/k_B T], \qquad (1)$$

with $A$ determined at high temperature and all temperature dependence associated with $U/k_B T$, the data of Figs. 1 and 2 yield $U = 0.12$ eV for 213 K $\leq T \leq$ 300 K and $U = 0.17$ eV for 180 K $\leq T \leq$ 205 K. These values are in good agreement with previous determinations from the dc conductivity.[12] In what follows we explain the observed size and temperature dependence of the change in $U$ in the critical regions.

To discuss these properties we propose a classical many-body theory whose validity extends beyond the area of solid electrolytes. The theory treats diffusive transport by mobile ions hopping among the interstices of an embedding lattice, and includes the effects of interactions among the diffusing ions. The conductivity changes accompanying ordering in $RbAg_4I_5$ exemplify processes in which interaction among mobile defects affect their mobility. In the interest of brevity, the treatment that follows is particularly adapted to this specific problem. A more complete account will be published elsewhere.[13]

For a particular distribution of the interstitials among the available sites in real space, the representative point of the system lies within a small volume $\gamma$ of configuration space.[14] A diffusion jump causes this point to pass through the surface separating $\gamma$ from a neighboring volume $\gamma'$ associated with the new distribution. A system initially prepared within $\gamma$ makes transitions from $\gamma$ to $\gamma'$ at a thermal mean rate given exactly[14] by

$$w_{\gamma\gamma'} = (2\pi k_B T/\hbar)\{G_{\gamma\gamma'} - G_\gamma\}, \qquad (2)$$

in which we employ the notation $\{G\} \equiv \exp(-G/k_B T)$. In Eq. (2), $\{G_\gamma\}$ is an integral of the distribution function $\rho$ over the volume $\gamma$, and $\{G_{\gamma\gamma'}\}$ is the unit distance multiplied by the integral of $\rho$ over the boundary separating $\gamma$ and $\gamma'$. The total rate $W$ at which jumps occur in the entire system is obtained by multiplying $w_{\gamma\gamma'}$ by the probability

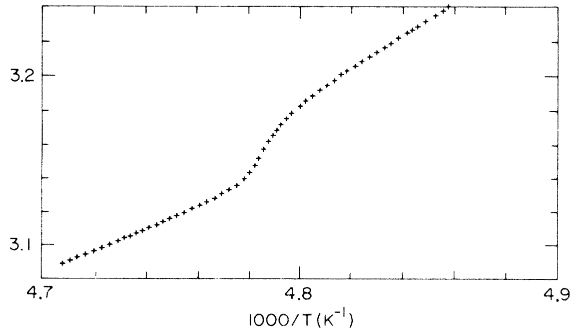

FIG. 1. Arrhenius plot of the sample resistance near 209 K as obtained by numerical integration of the $dR/dT$ measurements.

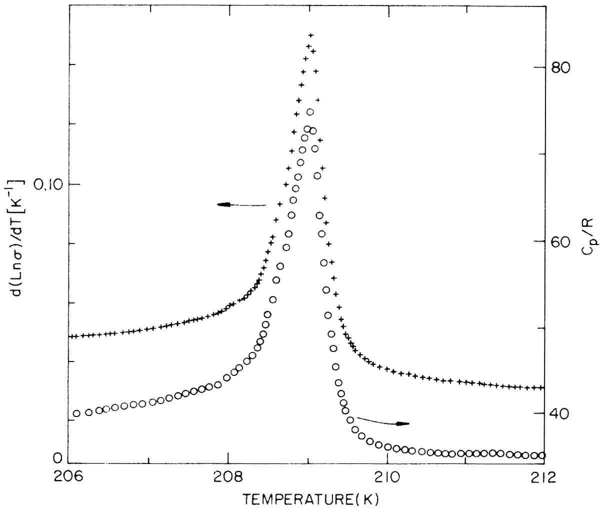

FIG. 2. Temperature derivative of $\ln\sigma$ vs temperature for $RbAg_4I_5$, with the molar heat capacity shown for comparison.

$\{G_\gamma\}/\sum_\gamma'\{G_\gamma\}$ that $\gamma$ be occupied, and summing over all (distinguishable) configurations, to find

$$W=(2\pi k_{\mathrm{B}}T/\hbar)\sum_{\gamma\gamma'}{}'\{G_{\gamma\gamma'}\}/\sum_{\gamma}{}'\{G_\gamma\}, \tag{3}$$

in which the prime on the summation marks the physical requirement of distinguishability.

The classical distribution function $\rho$, from which $G_\gamma$ and $G_{\gamma\gamma'}$ are derived, contains the many-body potential of interaction $V(\vec{s})$ among all host and interstitial atoms, with $\vec{s}$ the vector of mass-weighted coordinates locating all atoms. We write $V(\vec{s})=V^0(\vec{s})+V^i(\vec{s})$ in which $V^0(\vec{s})$ describes the lattice energy for uniform occupancy of the interstitial sites and $V^i(\vec{s})$ contains the remaining interactions among interstitials. To calculate $G_\gamma$ when $V^i$ is neglected, we expand $V^0(\vec{s})$ to second order in a Taylor series around its minimum value $V_\gamma{}^0$ at $\vec{s}_\gamma$. The resulting value,[14] which we call $G_\gamma{}^0$, is just $V_\gamma{}^0$ plus terms involving the frequencies of the normal modes that diagonalize $V^0(\vec{s})$ near $\vec{s}_\gamma$. We now switch on the interaction potential $V^i$ and, assuming that it varies smoothly with $\vec{s}$, include only the first two terms of its Taylor expansion around $\vec{s}_\gamma$. The important point of this linear approximation is that the mode frequencies do not change. It follows that the interactions influence $G_\gamma$ only to the extent of an additive potential $V_\gamma{}^i$ $[\cong V^i(\vec{s}_\gamma)]$. Analogous arguments show that $G_{\gamma\gamma'}{}^0$, also, is merely augmented by an additive potential $V_{\gamma\gamma'}{}^i$ at the saddle point. The crystal problem is thus transformed into a combinatorial problem of site occupancy.

For simplicity, we specialize to a case in which all sites and saddle points of $V^0$ are equivalent, with $G_{\gamma\gamma'}{}^0-G_\gamma{}^0=\hat{g}$ independent of the cell $\gamma$. Then

$$W=(2\pi k_{\mathrm{B}}T/\hbar)\times\{\hat{g}\}\sum_{\gamma\gamma'}{}'\{V_{\gamma\gamma'}{}^i-V_\gamma{}^i\}\{G_\gamma\}/\sum_{\gamma}{}'\{G_\gamma\}, \tag{4}$$

or

$$W\simeq(2\pi k_{\mathrm{B}}T/\hbar)\nu\{\hat{g}\}\{\langle V_{\gamma\gamma'}{}^i\rangle-\langle V_\gamma{}^i\rangle\}, \tag{5}$$

with $\langle\ldots\rangle$ representing the thermal average. In Eq. (5), $\nu$ is the mean number of saddle points $(\gamma\gamma')$ available to the individual configurations $\gamma$.

To evaluate Eq. (5) we still require detailed information about the interactions among interstitials. We postulate that, for accessible saddle points, neither site terminating the jump path is occupied by a second interstitial; otherwise, the jump is blocked, with $V_{\gamma\gamma'}{}^i\to\infty$. Then, for $\mathrm{RbAg_4I_5}$, with approximately tetrahedral coordination of $N$ sites containing $2N/7$ ions, we find $\nu\simeq 2N$ to second order in the inhomogeneities of the distribution among sites.[15] Further, for a potential function $V^i$ derived from pairwise interactions among the interstitials, $\langle V_\gamma{}^i\rangle$ is just $2h$, with $h$ the enthalpy of interaction per interstitial. Finally, we know little about the interaction potential $V_{\gamma\gamma'}{}^i$ at the saddle point. However, of necessity, an ion at the saddle point samples the short-range order of both an occupied site from which it originated and an empty site to which it may hop. Since it therefore couples less strongly to the local order, we write $\langle V_{\gamma\gamma'}{}^i\rangle=\mu\langle V_\gamma{}^i\rangle$ (anticipating that $|\mu|\ll 1$ and is almost independent of the precise local order) to obtain, finally, for the rate at which each interstitial jumps,

$$W=(4\pi k_{\mathrm{B}}T/\hbar)\exp\{-[\hat{g}-2(1-\mu)h]/k_{\mathrm{B}}T\}. \tag{6}$$

The Nernst-Einstein equation[16] then leads directly to the conductivity, from which we obtain, neglecting any possible dependence of the correlation factor on short range order,

$$d(\ln\sigma)/dT=2(1-\mu)c_p/k_{\mathrm{B}}T_c+B\quad(T\approx T_c), \tag{7}$$

with $c_p=(\partial h/\partial T)_p$ the heat capacity per particle of the mobile-ion subsystem, and $B$ containing all nonsingular contributions. We emphasize that Eq. (7) includes an accurate description of local order, and avoids mean-field-type approximation entirely.[3,7]

Having simultaneously measured the specific heat and conductivity in the vicinity of $T_c$ we are now in a position to examine their relative critical behavior without reference to fitting functions, exponents, or even a choice of $T_c$. In accordance with Eq. (7), the experimental values of $d(\ln\sigma)/dT$ are plotted in Fig. 3 as a function of the molar specific heat $C_p$ with the temperature as an implicit variable. The curves cover three decades of reduced temperature above and below the peak. No attempt has been made to subtract the temperature-dependent portion of the lattice heat capacity, and this undoubtedly causes some deviations of the curve from linearity far from the peak (at small values of $C_p$). The solid line fitted to the data above and below $T_c$ gives

$$d(\ln\sigma)/dT=(0.6105/RT_c)(C_p-24.09R). \tag{8}$$

It is evident from these results that experiment and theory are in good agreement and that the conductivity anomaly does indeed arise from changes in the ordering enthalpy at the transition. If all sites took part equally in the diffusion, $C_p$ should be apportioned equally among all four Ag

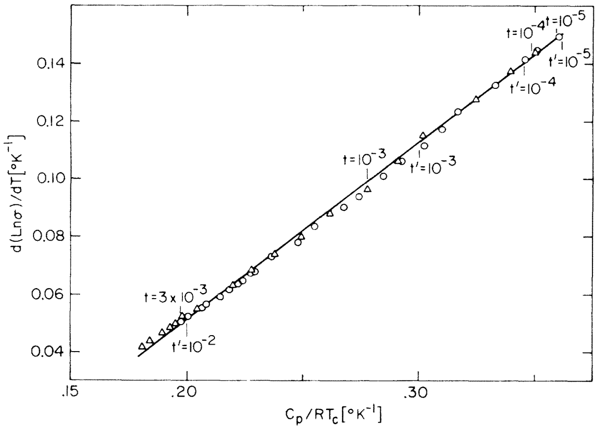

FIG. 3. Temperature derivative of ln$\sigma$ vs the molar heat capacity. Temperature is an implicit variable. Marks show decades of the reduced temperature $t = T/T_c - 1$ and $t' = 1 - T/T_c$. Triangles, $T > T_c$; circles, $T < T_c$.

ions per formula unit, so that $c_p/k_B = C_p/4R$. If, on the other hand, the transport occurred only through those sites that order, involving a fraction $\frac{3}{8}$ of the mobile ions,[8] then $c_p/k_B = 2C_p/3R$. These two assumptions yield, respectively,

$$2(1-\mu) = 2.44; \quad \mu = -0.22 \text{ (all ions)},$$

$$2(1-\mu) = 0.92; \quad \mu = 0.54 \text{ } (\tfrac{3}{8} \text{ of ions}).$$

Mobility processes in the real crystal are complicated but fall in between the stated extremes: The ordering sites are at least involved in every diffusive jump. It is therefore most satisfying that *the two values of* $\mu$ *average close to zero.* Apparently, the saddle points are, as expected, well isolated from the short-range order in the lattice. Changes in conductivity then occur because increasing *local* order deepens the potential well in which each ion sits, thereby increasing the activation energy as the system orders. We note that some error is introduced into Eq. (7) by our present neglect of any residual dependences of the diffusion correlation factor and the atomic frequencies on the precise degree of local order.[17] However, these effects are apparently quite negligible since data from above and below the transition superpose accurately (cf. Fig. 3).

It may be remarked in summary that, although the problem of ordering in interstitial solid solutions is an old one, a precise experimental and theoretical description of the mobility change induced by the ordering transformation has previously been lacking.[3,7] We expect that behavior similar to that described here can be observed for metallic hydrides and for ordering near other solid-state transitions.[5,6] In a larger view the present work establishes unambiguously that the critical behavior of the mobility is but one manifestation of a more general result, Eq. (7), connecting mobility and the interaction potential in dense systems of interacting mobile defects.

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