Low-Temperature Specific-Heat Anomaly of a One-Dimensional Ionic Conductor

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We report measurements of the specific heat of the one-dimensional ionic conductor hollandite for temperatures between 0.07 and 3 K. An anomalous contribution is observed which exhibits a pronounced peak unlike most disordered systems. The peak height strongly depends on the concentration of the diffusing ions. A theoretical interpretation is given.

Despite the large amount of work of the last years[1-3] a microscopic description of the low-temperature extra specific heat of amorphous materials has not yet been achieved. This problem has received further interest from the measurements of analogous effects in the ionic conductor β-alumina.[4] The phenomenological model consistent with various observations (specific heat, ultrasonic properties,[5] etc.) is based on the assumption that certain atoms or groups of atoms reside in a double-well potential giving rise to two-level systems.[6,7] In addition, the occurrence probability of various energy gaps has to be smooth for small gaps in order to reproduce the quasilinear behavior of the specific heat. The main questions concern (a) a microscopic description of the tunneling "particle" between the two levels; (b) the origin of very small gaps ($\cong 1$ K); (c) the nature of the smooth distribution.

In order to elucidate these points one should consider disordered systems for which microscopic information about the structure is available. In this respect the observation of anomalies in ionic conductors similar to those of other amorphous systems is of particular interest because these materials are rather well characterized microscopically. The basic model is that of a periodic potential (due to the host lattice) whose wells are partly filled by the interacting diffusing ions. A very suitable substance in this respect is the one-dimensional ionic conductor hollandite[8] ($K_{2\rho}Mg_{\rho}Ti_{8-\rho}O_{16}$ with $0.75 \lesssim \rho \lesssim 1$). In this compound the mobile K^+ ions reside in a periodic potential which is substoichiometrically occupied, and which does not communicate with neighboring channels. Through the analysis of diffuse x-ray scattering it was possible to obtain a good de-

scription of the state of order of the ions.[8,9] Each channel contains one site per unit cell along the c axis and the fractional occupancy of these sites with K^+ ions is equal to ρ. A very important role is played by the ion-ion interaction within each channel. Without this interaction the ions would be located at the local well minima. The ion-ion interaction removes the degeneracy of the energies of different configurations and causes the equilibrium position of the ions to shift from the minima of the background potential. This situation can be described by the Frenkel-Kontorova model with a finite density of defects.[9-11] The two parameters of the model have been determined for hollandite from the analysis of the structure factor $S(k)$.[9] We have therefore a precise formulation of a problem of *intermediate disorder*, the disorder being only that of the diffusing ions while the cage ions are assumed to give rise to the periodic potential. The configurational excitations of this system have been studied in some detail.[11] A configurational transition can be visualized as the hop of an ion into an empty site including the relaxation of all the other ions. The tunneling particle is therefore the jumping ion "dressed" with the relaxation of the other ones. Previously it has been shown that it is possible to obtain very low energy gaps for these excitations but their energy spectrum is always *discrete*.[11,12] As a consequence the specific heat of such a system is heavily structured; it consists of a series of peaks at temperatures corresponding to the characteristic energy gaps. As shown in Ref. 11, for hollandite the most prominent structure is expected to consist of a peak at $T \gtrsim 40\,°K$. Unfortunately this contribution is completely masked by the relatively large and struc-

tured phonon contribution to the specific heat of hollandite in this temperature range.

To explore configurational contributions at lower temperatures we have measured the specific heat of two hollandite samples with $\rho_1 \cong 0.77$ (± 0.005) and $\rho_2 \cong 0.78$ at very low temperatures, i.e., between 0.07 and 3 K. The measurements were made in a dilution refrigerator. The total weight of the samples was about 100 mg each. The specific heat C is plotted in Fig. 1 as a function of temperature. It differs markedly from the behavior found in amorphous solids[1-3] and β-alumina.[4] In our case the specific heat first rises much faster than linear and then at about 1 K exhibits a broad peak. This is found for both concentrations. However the magnitude of the specific-heat peak for the two systems differs by about a factor of 4. Such a striking dependence on the ionic concentration calls for special attention. We discuss now the interpretation of the observed anomalous specific heat in terms of the above-mentioned model.

Let us start by defining an array of length n as a series of n consecutive wells occupied by ions preceded and followed by empty wells. For high density of ions ($\rho \gtrsim 0.75$) we can neglect the occurrence of two (or more) empty wells adjacent to each other.[9] A configuration is then specified by the set of array lengths $\{n\}$. For example the configuration $\{n\} = 4; 3; 3; \cdots$ indicates that we have a vacancy, then *four* occupied wells, a vacancy, *three* occupied wells, a vacancy, *three* occupied wells, etc. In Ref. 9 it has been shown that the total static energy of a given configuration (including of course the ionic relaxation in each well due to the ion-ion interaction) can conveniently be written in terms of a spin-type Hamiltonian with an *effective long-range* interaction acting only between *empty sites*:

$$V = \sum_{j<j'} C(n^*)\sigma_j\sigma_{j'}; \quad C(n^*) = J\alpha^{n*}, \quad (1)$$

where J and $\alpha(<1)$ are related to the original parameters of the model (see Refs. 11 and 12). The variable σ_j assumes the value 0 or 1 if the jth site is, respectively, occupied or empty and n^* is the total number of occupied sites between the sites j and j'. The sum extends to *all* pairs of holes.

Numerical studies on a finite ring[11] with a density $\rho = \frac{3}{4}$ and using parameters appropriate to hollandite show a structure in the configurational specific heat at $T \gtrsim 40\,°K$ due to transitions of type $\cdots; 4; 4; \cdots - \cdots; 3; 5; \cdots$. The characteris-
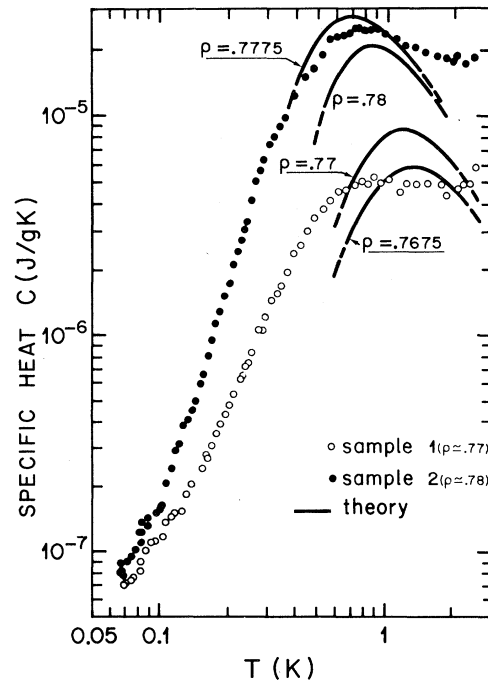

FIG. 1. Measured specific heat for two hollandite samples with slightly different ionic concentrations. The theoretical curves are computed as discussed in the text and with the parameters $C_I = 0.74$ eV (Ref. 9) and $J_0 = 0.30$ eV. The peak positions and the change of intensity as a function of concentration are in good agreement with the measured values. Only the total intensity was scaled because of the effect of blocking impurities.

tic gap between these two configurations can be estimated from Eq. (1) by limiting the interaction to the nearest holes[12]:

$$\Delta_1 \cong C(3) + C(5) - 2C(4) = J\alpha^4(\alpha + 1/\alpha - 2). \quad (2)$$

For pairs of states that are degenerate with respect to the interaction between nearest holes, such as $\cdots; 3; 4; \cdots - \cdots; 4; 3; \cdots$, we have to specify the configurations in more detail. Including the interaction up to second nearest holes, a transition like

$$\cdots; 4; 3; 4; 3; \cdots - \cdots; 4; 4; 3; 3; \cdots \quad (3)$$

has a characteristic gap

$$\Delta_2 \cong C(6) + C(8) - 2C(6) = \alpha^3\Delta_1 \quad (4)$$

which, since $\alpha \cong 0.3$,[11,12] is about 40 times smaller than Δ_1 and gives rise to a specific-heat peak at $T \sim 1-2\,°K$. It was not possible to detect these small gaps in Ref. 11 because of the small size of the system considered there. An analytical study

of the thermodynamics of infinite systems that is able to take into account these fine effects has been described in Ref. 12. The theoretical curves shown in Figs. 1 and 2 are computed with this method. The parameters used are based on the analysis of $S(k)$ at room temperature.[9] The only change, to optimize the agreement with experiments in Fig. 1, is in the value[9] of J_0 (barrier height of the background potential) from 0.23 to 0.30 eV. In fact, because of anharmonicity, we can expect that the apparent force constant (related in our model to J_0) is larger at lower temperatures.

In order to understand the strong concentration dependence of the specific heat we have to look at the transitions that give rise to the peak [Eq. (3)]. It is easy to see that the probability of having in the ground state a series of values like the starting configuration of Eq. (3) ($\cdots$; 4; 3; 4; 3; $\cdots$) is maximum if the arrays with $n = 3$ and $n = 4$ appear with equal probability. According to this simple argument the maximum peak height for the specific heat corresponds then to $\langle n \rangle = 3.5$ [$\rho = \langle n \rangle /$ $(\langle n \rangle + 1) = 0.7\underline{7}$] while the intensity goes to zero for $\langle n \rangle = 3(\rho = 0.7\overline{5})$ and $\langle n \rangle = 4(\rho = 0.80)$. These qualitative considerations are confirmed by the theoretical curve[12] reported in Fig. 2 which explains very well the peak height difference between the two samples. The sharpness of the curve in Fig. 2 indicates that the probability distribution for the position of various arrays is not random but quasiordered.

A problem arises in the comparison of the abso-

lute magnitude between the measured peak height and the theoretical one. In Fig. 1 we have simply scaled the absolute peak height, but the computed one is actually much larger than the experimental one. This is due to the fact that in the theory we treat the system as an infinitely long chain while we know that the actual samples contain a high density of blocking impurities[13] so that the real system is essentially a collection of separate segments of various lengths. A transition of the type described by Eq. (3) remains quasidegenerate and produces the low-temperature specific heat contribution only if a segment of about 30 wells (including ionic relaxation) is free of these blocking defects. This implies that only those segments that have a length of at least 30 wells can contribute to the specific-heat peak at ~1 K. The inclusion of this effect drastically reduces the theoretical peak height and we recover the experimental peak height if we assume the average separation between blocking barriers to be about ten lattice sites. This assumption is in quantitative agreement with the conductivity data.[13]

In summary we believe this is the first time that the low-temperature specific heat anomalies of a disordered system have been analyzed in terms of a *microscopic* model. In agreement with the theoretical results the experiments confirm that the disorder due to diffusion (interacting) ions in an otherwise periodic potential can give rise to very low energy gaps for configurational excitations but not to a smooth distribution of these energies. From preliminary calculations we think this to be the case also in higher dimensions so that the quasilinear specific heat observed in β-alumina has to be linked to additional sources of disorder such as, for example, that due to the compensating ions. A similar effect is probably the cause of the smooth background structure that seems to be present in the hollandite data in addition to the peak and that is most visible near 0.1 K.
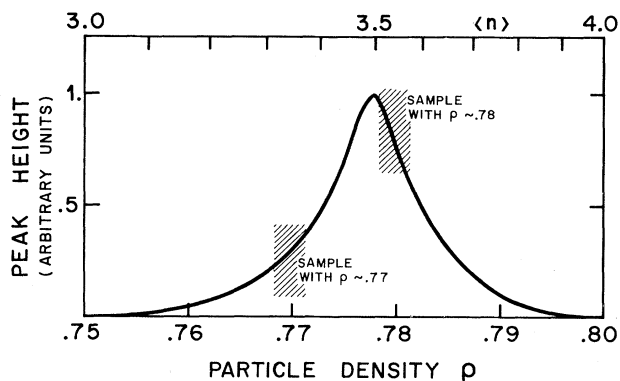

FIG. 2. Magnitude of the computed low-temperature specific-heat peak height as a function of the ionic concentration. As expected from the arguments reported in the text, the maximum is at $\langle n \rangle = 3.5$ ($\rho = 0.7\underline{7}$) and the intensity goes to zero for the two "commensurate" cases $\langle n \rangle = 3$ ($\rho = 0.75$) and $\langle n \rangle = 4$ ($\rho = 0.80$).

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Theory of the Blue Phase of Cholesteric Liquid Crystals

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We present a theory of the cholesteric blue phase, assuming a first-order cholesteric-isotropic transition. We show, on the basis of the Oseen-Frank elasticity equations, that the planar helix structure, generally associated with the cholesteric phase, becomes unstable at temperatures near the transition point. It transforms into a phase characterized by a network of disclination lines.

In many cholesteric liquid crystals the transition between the regular helical cholesteric phase and the isotropic phase occurs through one or more intermediate phases. These are the cholesteric "blue phases," which are thermodynamically stable over a narrow temperature range, often less than 1 °C. Recently, there has been a renewed interest in the study of the blue phases,[1-10] largely stimulated by a theoretical explanation for their existence by Brazovskii.[11-13] From the observation of Bragg reflections at visible wavelengths,[7,10] it is now well established that at least in some cases the blue phases have a structure of cubic symmetry, with unit-cell dimensions of the order of the cholesteric pitch.

Attempts at a theoretical treatment of the blue

phases[11-13] have been based on Landau theory. This theory predicts a phase in which the order parameter is locally biaxial in large regions of the unit cell of the cubic material. In addition, the theory appears to be difficult to use in predicting more than one blue phase whereas experimentally there are known to be up to three separate phases. Moreover, the important parameter of the theory for estimating when the predicted phase is stable is $Kq_0^2/l(\Delta T/T_1)$, where K is a typical elastic constant, q_0 is 2π divided by pitch, l is the latent heat of the first-order transition, and $\Delta T = (T_c - T_1)$, with T_c the extrapolated second-order transition temperature and T_1 the first-order transition temperature. This ratio is just the elastic energy associated with the twist di-