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LOW-TEMPERATURE SPECIFIC HEAT ANOMALY OF THE ONE-DIMENSIONAL IONIC CONDUCTOR HOLLANDITE

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Most amorphous materials contain localized excitations which strongly influence their low temperature properties; for example, for temperatures below a few K the specific heat varies almost linearly with temperature, and the thermal conductivity is drastically reduced compared to crystalline materials and generally exhibits a T^2 dependence /1/. It is now accepted that these excitations arise from tunnelling of certain parts of the disordered network between two potential energy minima /2/. However, the question of the microscopic origin of the tunnelling systems has not been solved yet. Similar properties have been observed in superionic conductors /3/, and this seems to be particularly promising in order to elucidate the microscopic origin of these excitations because in superionic conductors the disorder can be reduced to two dimensions or even to one dimension. We have therefore carried out specific-heat measurements in the one-dimensional superionic conductor hollandite and we explain its specific heat in terms of a microscopic model.

In hollandite ($K_{2x}Mg_xTi_{8-x}O_{16}$), the mobile K^+ ions reside in a linear periodic potential which is substoichiometrically occupied. The channels containing the K^+ ions do not communicate with neighbouring channels. By analysis of diffuse X-ray scattering a good description of the state of order has been obtained /4/. 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 x. Very important is the ion-ion interaction within each channel: it removes the degeneracy of the energies of different configurations and causes the equilibrium position of the ions to shift from the local minima of the background potential. The question is: what are the configurational states in such a system and how do they contribute to the specific heat /5/? Specific-heat measurements have been carried out in two samples with $x = 0.77$ and $x = 0.78$ at temperatures between 70 mK and 3 K. The measurements were made in a dilution refrigerator using samples weighing about 100 mg each, and the results are plotted in Fig. 1 as a function of temperature. The specific heat first increases rapidly with temperature and then exhibits a maximum at .8 K for $x = .78$ and at 1 K $x = .77$. The overall behaviour differs markedly from that found in glasses /2/ and in β -alumina or LiN_3 /3/. Furthermore, it is very striking that a difference of only 1% in x causes the specific heat to change by a factor of four. Such a drastic effect calls for special attention.

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Let us start the discussion of the specific heat by defining an array of length n as a series of n consecutive wells occupied by ions which are surrounded by empty wells. For sufficiently high density of ions ($x \geq .75$) we can neglect the occurrence of two or more empty wells adjacent to each other. A configuration is then specified by the set of array lengths $[n]$, e.g. $[n] = 4;3;3;\dots$ indicates that we have a vacancy, then four occupied wells, a vacancy, three occupied wells etc. It has been shown that the total potential energy of a given configuration including the contribution of the ionic relaxation in each well due to the ion-ion interaction can be written in terms of a spin type Hamiltonian acting only between empty sites /4/:

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

Here J and $\alpha (\leq 1)$ are parameters related to the barrier height of the background potential and to the strength of the ion-ion interaction. The variable σ_j assumes the value 0 or 1 depending on whether the j -th site is 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 empty sites. With $x=.77$ and using parameters appropriate to hollandite, a contribution to the specific heat $T \geq 40$ K is expected due to transitions of type $\dots;4;4;\dots \rightarrow \dots;3;5;\dots$. The energy difference Δ_1 between these two configurations can be estimated from Eq. (1) limiting the interaction to nearest holes /4,6/:

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

However, for pairs of configurations that are degenerate with respect to the interaction between nearest holes like $\dots;3;4;\dots \rightarrow \dots;4;3;\dots$ the interactions up to second nearest empty wells must be included. Transitions like $\dots;4;3;4;3;\dots \rightarrow \dots;4;4;3;3;\dots$ might occur which have a characteristic gap $\Delta_2/6$:

$$\Delta_2 = C(6) + C(8) - 2C(7) = \alpha^3 \Delta_1 \quad (3)$$

Because $\alpha \approx .3$, Δ_2 is about 40 times smaller than Δ_1 and gives rise to a specific heat peak at $T \approx 1-2$ K which agrees nicely with the experimental findings.

In order to understand the strong concentration dependence of the specific heat we need to take a closer look at the transitions that give rise to the peak. The probability of having a series of values like the starting configuration of Eq. (3) in the ground state is maximum if arrays with $n=3$ and $n=4$ appear with equal probabili-

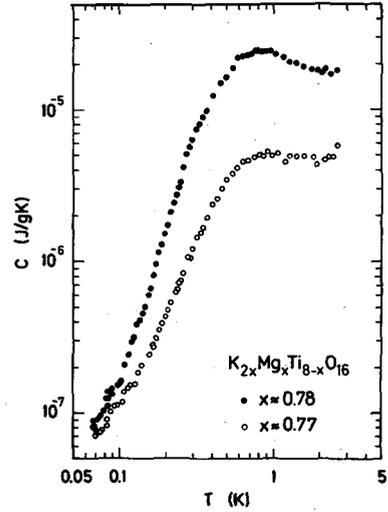


Fig.1: Specific heat of hollandite

ty. According to this argument the maximum specific heat is obtained for $n = 3.5$ ($x = \langle n \rangle / (\langle n \rangle + 1) = .77$) whilst it tends to zero for $\langle n \rangle = 3$ ($x = .75$) and $\langle n \rangle = 4$ ($x = .80$). For intermediate values of x a more detailed treatment is necessary, which, in fact, reproduces the strong variation of the specific heat by a factor of 4/6/.

Comparing the absolute magnitude between the measured specific heat and the theoretical expected one we find that the theoretical curve is much larger. This is due to the fact that the system has been treated as an infinitely long chain, while the actual samples contain a high density of impurities so that the real system is a collection of separate segments of various lengths. The inclusion of finite chain length into theory drastically reduces the magnitude of the specific heat and we recover the experimental value if we assume the average separation between blocking ions to be about 10 lattice sites.

A further interesting question is how the transition actually occurs. In the model discussed above a configurational transition can be regarded as the hop of an ion into an empty site including the relaxation of all other ions. The tunnelling particle is therefore the jumping ion accompanied by the other relaxing ions. Taking an effective barrier of about 0.04 eV between the configurational states /4/ and taking the formula for relaxation due to tunnelling, we estimate a relaxation time τ which is at least of the order of seconds at $T \approx 1$ K. This value is rather uncertain owing to the unknown parameters describing the degree of overlap of the wavefunctions needed to calculate τ . For comparison, the classical relaxation time (Arrhenius law) at this temperature would be of the order of 10^3 years.

In summary, we should like to point out that the low-temperature specific heat anomalies of a disordered system have been analyzed in terms of a microscopic model. Experiment and theory confirm that the disorder due to diffusing and interacting ions in an otherwise periodic potential can give rise to very low energy excitations but not to a continuous distribution of excitations. The transition between the states occurs via tunnelling.

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