Anomalous behaviour of the low-temperature heat capacity for KCl crystals with heavy univalent impurities

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Anomalous behaviour of the low-temperature heat capacity for KCl crystals with heavy univalent impurities

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Résumé. — De faibles concentrations d'impuretés lourdes et monovalentes Cs^+ et I^- ont pour conséquence une augmentation de la chaleur spécifique de KCl à basse température. Ce comportement anormal a été expliqué à l'aide d'une théorie utilisant une fonction de Green, pour de faibles concentrations. Les calculs ont été effectués grâce à un modèle de perturbation localisée qui inclut un changement de masse sur le site de l'impureté aussi bien qu'un changement des constantes de forces radiales avec les plus proches voisins. Un accord raisonnable est obtenu avec les données expérimentales. La contribution du défaut de masse est de 80 % du changement de la chaleur spécifique ; la contribution restante est due aux changements de constante de force. Les contributions les plus importantes au changement de chaleur spécifique sont due aux modes impairs de symétrie F_{1u}. La partie réelle du dénominateur de résonance dans la représentation irréductible F_{1u} donne une fréquence quasi localisée. La valeur trouvée de la fréquence de résonance dans le cas de KCl : I^- est voisine de celle obtenue précédemment par l'étude de la conductivité thermique du même système.

Abstract. — The effect of low concentrations of heavy univalent Cs^+ and I^- impurities on the low-temperature heat capacity of KCl gives an enhancement in the heat capacity. This anomalous behaviour has been explained on the basis of a low concentration Green's function theory. A localized perturbation model which includes mass change at the impurity site as well as changes in the nearest neighbour radial force constants has been employed in performing the calculations. Reasonable agreement with the experimental data is obtained. The mass defect contribution is found to be 80 % of the changed specific heat and the remaining contribution is due to force constant changes. The main contributions to the changed specific heat is caused by odd parity F_{1u}-symmetry modes. The real part of the resonance denominator in F_{1u}-irreducible representation gives a quasi localized frequency. The present value of the resonant frequency in case of KCl : I^- is seen to be similar to those obtained earlier in the study of thermal conductivity of the same system.

1. **Introduction.** — One of the most important properties of a crystal where the frequency spectrum plays a central role is the lattice specific heat. At low temperatures the high-frequency localized modes are not excited. At high temperatures a significant number of local modes are excited but all other phonons of the lattice are also excited. Thus the local modes will induce a relatively small change in the large total specific heat and the possibility of observing local modes in specific-heat measurements is very small. On the other hand, low-frequency resonance modes get excited even at low temperatures and can be observed in specific-heat experiments. Lehmann and de Wames [1], Kagan and Iosilevskii [2], Karlsson and present authors [3-5] have shown that the contribution of resonance modes to the lattice specific heat may be appreciable at low temperatures. Quite recently some combined experimental and theoretical studies have been made for the temperature dependence of the lattice specific heat of crystal containing small concentration of impurities.

Recently, Kvavadze and Augst [6] performed an experiment and found that the low temperature specific heat of KCl crystals increased as a result of introduction of Cs^+ and I^- impurities. They have discussed the experimental results on the basis of a theory of Kagan and Iosilevskii [2] using a Deby frequency spectrum for the host lattice, but their theoretical results were very poor.

In the present work we have employed realistic models both for the defect perturbation and the host KCl and have determined the contribution of impurities to the specific heat of KCl. The present impurity model is a point-ion model in which the change in mass at impurity site and the change in nearest neighbour central force constant is considered. The results of the lattice dynamics of KCl in the deformation dipole model have been used in the calculations. Numerical computations for specific heat have been performed for the two impurity systems of KCl : Cs^+

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and KCl : I⁻ containing 1.4 mole % Cs⁺ and 1.8 mole % I⁻, respectively.

2. Theory. — 2.1 LATTICE SPECIFIC HEAT. — The lattice specific heat of a solid per g mol is given by (for details see reference [3])

$$C_L(T) = \frac{\hbar^2}{4 \, k_B \, T^2} \int_0^\infty \omega^2 \, N(\omega) \cosh^2 (\hbar\omega/2 \, k_B \, T) \, d\omega \,,$$

$$(1)$$

where T is the temperature, $\hbar$ is the Planck constant, k_B is Boltzmann constant and $N(\omega)$ is number of phonon states lying in the interval ω and $\omega + d\omega$ as $d\omega \to 0$.

The introduction of impurities changes the phonon density of states. Accordingly the lattice specific heat is also changed. If we assume that the perturbation is symmetric, the phonon density of states can be expressed as the sum of the contributions from the various irreducible representations. The change in the specific heat can thus be expressed as

$$\Delta C_L(T) = \sum_\nu \Delta C_L^\nu(T) \qquad (2)$$

where $\Delta C_L^\nu(T)$ is the change in specific heat in the irreducible representation ν.

The phase shifts can be defined as

$$\tan \delta_\nu = - \frac{\text{Im} \, D_\nu(z)}{\text{Re} \, D_\nu(z)} . \qquad (3)$$

Here $D_\nu(z) = |\mathbf{I} + \mathbf{g}_\nu(z) \, \mathbf{P}_\nu(\omega^2)|$ is called the resonance denominator in the irreducible representation ν. $\mathbf{I}$ is the unit matrix and $\mathbf{g}_\nu(z)$ and $\mathbf{P}_\nu(\omega^2)$ are the Green functions and perturbation matrices projected into the subspace of irreducible representation ν and z is the complex squared frequency equal to $z = \omega^2 + i\eta$ in the limit $\eta \to 0$.

In low concentration limit we assume that the defects do not interact and the vibrational properties can be understood only by knowing the behaviour of a single impurity. Therefore, one may determine the change in specific heat due to a single defect and multiply it by the number of defects present in the solid.

After integrating equation (1) and introducing the phase shifts the change in lattice specific heat due to impurities turns out to be

$$\Delta C_L(T) = - \sum_\nu \frac{2 \, k_B \, cNB^2}{\pi} \int_0^\infty \delta_\nu \, \omega \cosh^2 (B\omega)$$

$$\times (1 - B\omega \coth (B\omega)) \, d\omega \,, \qquad (4)$$

where c is the fractional impurity concentration, N is the number of atoms per g mol in the host crystal, and $B = \hbar/2 \, k_B \, T$.

2.2 DEFECT PERTURBATION MODEL. — The nearest-neighbour perturbation model for a substitutional ion in a NaCl-type lattice has been described in previous works [7, 8]. The resonance denominators for an impurity are seen to be

$$D_{A_{1g}}(z) = 1 + 2 \, \lambda\chi(g_4 + 2 \, g_5) \qquad (5)$$

$$D_{E_g}(z) = 1 + 2 \, \lambda\chi(g_4 - g_5) \,, \qquad (6)$$

and

$$D_{F_{1u}}(z) = 1 - \varepsilon\omega^2 \, g_1 + 2 \, \lambda(g_1 + \chi g_3 - 2 \, \chi^{1/2} \, g_2) -$$

$$- 2 \, \varepsilon\omega^2 \, \lambda\chi(g_1 \, g_3 - g_2^2) \,, \qquad (7)$$

where $\chi = M_+/M_-$ is the ratio of the masses of two ions of an unit cell, λ is the change in the mass-reduced nearest-neighbour central-force constant, and ε is the mass change parameter equal to $(M'_\pm - M_\pm)/M_\pm$. $M'_\pm$ is the mass of the impurity.

3. Numerical computations and results. — The specific heat of KCl and KCl : 1.4 mole % Cs⁺ and KCl : 1.8 mole % I⁻ have been measured by Kvavadz and Augst [6]. An enhancement in the specific heat due to presence of impurities was observed. Equation (4) has been employed for calculating the change in the specific heat of KCl doped with Cs⁺ or I⁻ ions in the temperature range 3-20 K. The force-constant change λ was taken as a parameter to obtain best fits with the experimental data. In the calculation we have used the values of the five Green's functions computed earlier by Benedek and Nardelli [8] in Hardy's deformation-dipole model for KCl at 4 096 points in the first Brillouin zone.

The computed results are compared with the experimental data in figures 1 and 2 for KCl : Cs⁺ and KCl : I⁻ systems, respectively. In the beginning an attempt was made to fit the experimental data using only mass change, but was unsuccessful. The inclusion of λ was then necessary. In figures 1 and 2 we observe that an overall good agreement with experiment takes place for $\lambda = - 0.650 \times 10^{26} \, \text{s}^{-2}$ for Cs⁺ impurity and $\lambda = -0.532 \times 10^{26} \, \text{s}^{-2}$ for I⁻
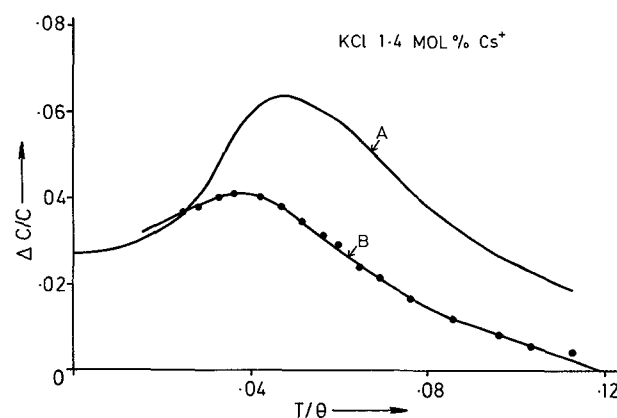

Fig. 1. — Enhanced specific heat in KCl : Cs⁺ system. (●) Experimental results. Curve A : $\lambda=0$; Curve B : $\lambda= -0.650 \times 10^{26} \, \text{s}^{-2}$.
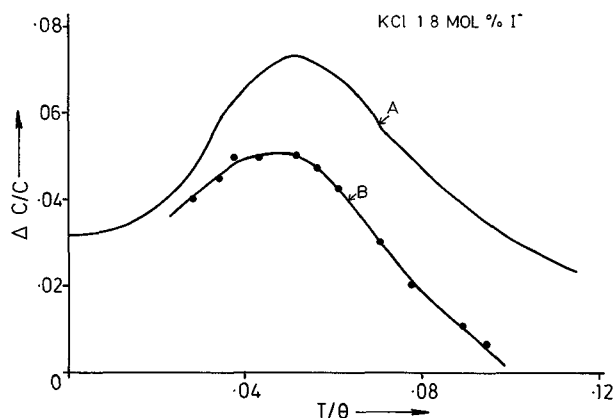
Fig. 2. — Enhanced specific heat in KCl : I⁻ system. (●) Experimental results. Curve A : $\lambda = 0$; Curve B : $\lambda = - 0.532 \times 10^{26} \text{s}^{-2}$.

impurity, respectively. The impurity contribution to the specific heat is very much sensitive to force constant change. For example a 10 % change in λ produces an average change for about 30 % in the whole temperature range of enhanced specific heat.

If we plot the real part of the resonance denominator in the F_{1u}-irreducible representation for

$$\lambda = - 0.650 \times 10^{26} \text{ s}^{-2}$$

for KCl : Cs⁺ system we see that a low frequency resonance appears at $\omega_r = 48.5 \text{ cm}^{-1}$. Whereas in the case of KCl : I⁻ systems we get the resonance in the symmetry mode at $\omega_r = 56.4 \text{ cm}^{-1}$. From thermal conductivly results we get the resonance frequency [9] at $\omega_r = 57 \text{ cm}^{-1}$.

The main contribution to the specific heat arises due to F_{1u} symmetry modes. The contributions of the two other irreducible representations A_{1g} and E_g are comparatively much smaller.

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