

Energy Eigen Value and Specific Heat for $\langle 111 \rangle - \langle 100 \rangle$ Tunneling Model

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Abstract : Within the framework of two parameter octahedral potential for a dipolar impurity in ionic crystals, it is possible for impurity to possess minimum-energy orientational configurations in two crystallographic directions simultaneously. Two possible combinations are $\langle 111 \rangle - \langle 110 \rangle$ and $\langle 111 \rangle - \langle 100 \rangle$. Taking second model here we have try to find out the expressions for energy eigen value and specific heat.

1. Introduction

The possibility of the existence of two sets of minimum-energy orientational configurations of the impurity in the matrix is interesting and exciting because leaving the ideal case of $\text{KCl} : \text{Li}^+$ systems which exhibits a perfect agreement with $\langle 111 \rangle$ off-centered model of Gomez *et al.*¹, most other paraelectric system present a difficulty in them. Initially Seward and Narayanamurti² show that impurity could have potential minima along any of the six $\langle 100 \rangle$ direction, but failed to explain the $\text{RbCl} : \text{CN}^-$ system, paraelectric resonance³ and specific heat⁴ at low temperature. After sometime Luty⁵ and Beyeler⁶ have done experiments on the stress induced splitting of the intramolecular vibration line which showed that the correct minimum energy orientational configuration of CN^- impurity in ionic crystals is along the one of the eight $\langle 111 \rangle$ direction, but failed to explain the double bump of $\text{RbCl} : \text{CN}^-$ system. Latter Quigley and Das⁷ said that there is possibility of potential minima along $\langle 111 \rangle$ direction, but at high field polarization and para electric cooling experiments of Rollefson⁸ are better fitted by the $\langle 110 \rangle$ off-center displacement model. Thus there are many examples where simple tunneling model are either unable to explain the observed results or partially explain. Latter Pandey *et al.*⁹ show that there are simultaneous potential minima along two crystallographic directions

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i.e. either $\langle 111 \rangle - \langle 110 \rangle$ or $\langle 111 \rangle - \langle 100 \rangle$ direction. First model explain many results but fails to explain $\text{RbCl} : \text{CN}^-$ system. Recently using this model Raj Kumar *et al.*¹⁰ explain the backward line of $\text{KI} : \text{OH}^-$ system. Here in this paper we have try to find out the energy eigen value and specific heat for $\langle 111 \rangle - \langle 100 \rangle$ tunneling model.

2. Theory

There were six equivalent $\langle 100 \rangle$, the eight equivalent $\langle 111 \rangle$ and twelve equivalent $\langle 110 \rangle$ states in paper of Gomez *et al.*¹. In present case there is a set of each of six and eight equivalent states of simultaneous occurrence of potential minima along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. The designation of states have given below.

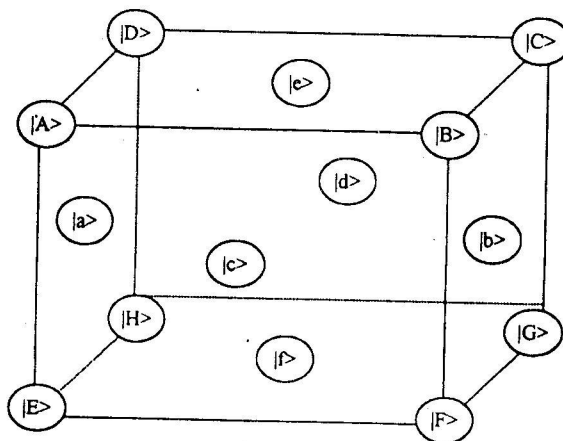


Figure : Pocket states for simultaneous potential minima along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions in the O_h symmetry group.

For a finite crystal field, there will be matrix elements of the Hamiltonian connecting the different states *i.e.* there will be finite probability of tunneling through the potential barrier to a new orientation. Here η connecting the states of $\langle 111 \rangle$ minima group to the nearest neighbour of same minima group, η^1 connecting the states of $\langle 100 \rangle$ minima group to the nearest of same minima group. Here we assume that the tunneling matrix element to the far off wells are insignificant compared to the tunneling matrix elements to the nearest neighbouring wells. There will be also a matrix element χ connecting the states of $\langle 111 \rangle$ minima group to $\langle 100 \rangle$ minima group. Hence we find a crystal field hamiltonian. H_0 which can be converted into H_0^1 by a proper transformation matrix by which energy eigen value and specific heat are calculated.

3. Expressions for Energy Eigen value

Using Hamiltonian H_0^1 we obtained the expressions for the energy eigen value for the model as follows :

$$\begin{aligned}
 & E(A_{1g} \text{ and } a_{1g}) \\
 (1) \quad & = \frac{p-3\eta-4\eta^1}{2} \pm \left[\frac{(p-3\eta+4\eta^1)^2}{2} + 6\chi^2 \right]^{1/2}
 \end{aligned}$$

$$\begin{aligned}
 & E(T_{1u} \text{ and } t_{1u}) \\
 (2) \quad & = \frac{p-\eta-2\eta^1}{2} \pm \left[\frac{(p-\eta+2\eta^1)^2}{2} + 4\chi^2 \right]^{1/2}
 \end{aligned}$$

$$(3) \quad E(T_{2g}) = \eta$$

$$(4) \quad E(T_{2u}) = 3\eta$$

$$(5) \quad E(e_g) = p + 2\eta^1$$

4. Expressions for Specific Heat

In present work we develop the defect contribution to the specific heat in a single and two multiplet tunneling model. Let ground state tunneling multiplet is split into p levels, then average energy to N impurity per unit volume at temperature T is given by :

$$(6) \quad E = \frac{N \sum_{i=1}^p g_i E_i e^{-E_i/KT}}{N \sum_{i=1}^p g_i E_i e^{-E_i/KT}}$$

where g_i is the degeneracy of the level and E_i is the energy splitting between the i^{st} and i^{th} level.

Hence, specific heat is given by following expression :

$$(7) \quad C_v = \frac{\partial \langle E \rangle}{\partial T}$$

Thus, the impurity contribution to the specific heat for the three single multiplet model are given as follows :

$$(8) \quad C_v = 6Nk\gamma^2 \left[\frac{e^{-2\gamma} + 3e^{-3\gamma} + e^{-5\gamma}}{(1 + 3e^{-2\gamma} + 2e^{-3\gamma})^2} \right]$$

For $\langle 111 \rangle$ model

$$(9) \quad C v = 6 N K y^2 \left[\frac{e^{-y} + 4 e^{-2y} + 6 e^{-3y} + 4 e^{-4y} + e^{-5y}}{(1 + 3 e^{-y} + 3 e^{-2y} + e^{-3y})^2} \right]$$

and for $\langle 110 \rangle$ model

$$(10) \quad C v = 6 N K y^2 \left[\frac{e^{-y} + 4 e^{-2y} + 18 e^{-3y} + 20 e^{-4y} + 5 e^{-5y}}{(1 + 3 e^{-y} + 3 e^{-2y} + 5 e^{-3y})^2} \right]$$

where $y = E / K T$.

Using above equations we can find out the expression of specific heat for $\langle 111 \rangle - \langle 100 \rangle$ tunneling model given below :

$$(11) \quad C v = 6 N K y^2 \left[\frac{e^{-y} + 5 e^{-2y} + 9 e^{-3y} + 4 e^{-4y} + 2 e^{-5y}}{(2 + 3 e^{-y} + 6 e^{-2y} + 3 e^{-3y})^2} \right]$$

5. Result and Discussion

The result of present theoretical investigation for the $\langle 111 \rangle - \langle 100 \rangle$ tunneling model are shown by equation (1) to equation (5) for energy eigen value and by equation (11) for specific heat. These result can be used for future theoretical investigation to explain anomalous results (like $\text{RbCl} : \text{CN}^-$ system) of various experimentally available system.

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