Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 979–983

ROTATIONAL STATES OF THE AMMONIUM ION IN CUBIC LATTICE

Y. Ozaki[*]

Department of Applied Chemistry, Nagoya Institute of Technology, Showa-ku,
Nagoya 466-8555, Japan

Abstract

The ammonium ion in the alkali halide lattice has the hindered rotational state. The rotational potential is expressed as crystal field, which depends upon only one rotational motion. The tetrahedral ion receives an octahedral field in this system. Four fundamental types of orientation appear due to the symmetry of ion and that of field. As the barrier height increases, the rotational levels approach to the librational levels with tunnel splitting. In particular, the tunneling part in the ground librational level is calculated using both free rotor bases and orientationally localized states. The level structure with the degeneracy is elucidated, which is peculiar in each type of orientation. Thermal properties are shown as model calculations.

Keywords: molecular orientation in solid phase, rotational tunneling states

Introduction

The rotational motion of the ammonium ion in KBr lattice was extensively examined using inelastic neutron scattering and the measurements of heat capacity [1]. In the analysis of symmetrical problem in the rotating ion, the tunneling system [2] derived from orientational pocket states was used to elucidate the most suitable orientation. In addition, Mukhopadhyay *et al*. [3] have proceeded to do inelastic neutron scattering and the dielectric measurements in several kinds of alkali halide (AX) lattice. They have found that changing the anion X^- or the cation A^+ in the host lattice give rise to the systematic energy shift. The difference in the ionic size seems to suggest promoting the reexamination of the model in tunneling. In this paper, we confine ourselves to only the thermal property in the tunneling system. Computational result is presented briefly.

Hindered rotation and molecular orientation

When the ammonium ion is put into AX lattice as impurity, the ion is replaced with the cation A^+. The NaCl type of lattice is retained in lower temperature. The rotating

---

[*] E-mail: ozaki@ks.kyy.nitech.ac.jp

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

system should be supposed to a rigid tetrahedral ion surrounded by nearest neighboring anions, which form one octahedron. Further neighbors in the lattice interact considerably with NH_4^+ ion because of the long-range Coulombic force. These additional interactions also have the octahedral symmetry. Therefore, the site symmetry of ammonium ion is determined according to the arrangement of the tetrahedron in the center of an octahedron.

The rotational potential is expressed by the octahedral functions as crystal field. They are the functions of Euler angle ω, which denote the molecular orientation. Due to the symmetry of this system first two terms in the expansion are given by fourth and sixth orders.

$$V(\omega)=\beta_4 V_4(\omega)+\beta_6 V_6(\omega) \tag{1}$$

The rotational Hamiltonian contains the kinetic part and this potential. Rotational energy levels are computed by solving eigenvalue problem under this Hamiltonian on the basis of free rotor functions. Generally, as the coefficients in the potential increase, the levels make bundles, which correspond to the torsional levels. Each torsional level splits into several ones even in quite strong field. This splitting is originated by the quantum tunneling on rotational motion.

The ratio of two coefficients in Eq. (1) determines the most stable orientation in the potential. We note that the sign of coefficients should be set up for certain. As the symmetry of surrounding is higher than the molecular symmetry, it is possible to take more than two equivalent orientations. The ion located in site has such orientation symmetry. In this system, the orientation symmetry is classified into four types called Td, D2d, C3v, and C2v. Each type includes N_0 members (N_0= 2, 6, 8, 12). One of members in any type consists of 2^4 spin states in tetrahedrally arranged proton system. Therefore, as the spin-rotational bases we may use $16N_0$ orientationally localized states. In the extreme strong field, the tetrahedron is much restricted around the localized state or pocket state. It is assumed that the most significant contribution to the tunneling mechanism comes from the one-dimensional rotation by the smallest angle. The connection through such rotational transfer provides the non-zero element a in the space of $16N_0 \times 16N_0$ matrix. Thus, the tunneling levels as eigenvalues are expressed in terms of the a-value. In Td, D2d, and C3v, the tunneling system yields 5, 7, and 11 levels, respectively. In practice, the above assumption concerning the transfer by only the smallest angle is supported by the calculation in the case of strong field from Eq. (1). As a comparison, the case of the tetrahedron in a tetrahedral cage (N_0=1) is also illustrated. Besides, the fourth type C2v is involved with the quite similar level structure as C3v, so that we will do not state about C2v from now on.

We practice the symmetrization process for the spin part in four protons. The symmetrized spins present the total spin I. There are three spin species: A, T, and E, which correspond to I=2, 1, and 0 in this order. In all types of tunneling, the ground state appears as an A-level, and the first excited state as a T-level.

Thermal properties in tunneling levels

Rotational tunneling levels in Td, D2d, and C3v symmetry are shown in Table 1. Two labels, such as $\overline{\mathrm{A}}_1\mathrm{A}_1$, mean the energy level. The former with bar comes from the symmetry of molecular part and the latter without bar that of spatial part, namely the symmetries in octahedral double group $\overline{\mathrm{O}}\mathrm{O}$. The tetrahedron in a tetrahedral field makes the similar levels as three levels in the lower part of Td type. In Td or C3v, the levels are exactly symmetrical about upper part and lower part.

Table 1 Tunneling levels of the tetrahedron in octahedral field. The eigenvalues from localized states are given by *a* (the value in matrix element) and the degeneracy is due to the spin-rotational state

Level in $\overline{\mathrm{O}}\mathrm{O}$	Eigenvalue/*a*	Degeneracy
(1) Td		
E_1 ($\overline{\mathrm{A}}_1\mathrm{A}_1$)	6	5
E_2 ($\overline{\mathrm{T}}_1\mathrm{T}_1$)	2	9
E_3 ($\overline{\mathrm{E}}\mathrm{E}$)	0	4
E_4 ($\overline{\mathrm{T}}_2\mathrm{T}_2$)	–2	9
E_5 ($\overline{\mathrm{A}}_2\mathrm{A}_2$)	–6	5
(2) D2d	$c=\sqrt{17}$	
E_1 ($\overline{\mathrm{A}}_1\mathrm{A}_1$)	8	5
E_2 ($\overline{\mathrm{T}}_1\mathrm{T}_1$)	$1+c$	9
E_3 ($\overline{\mathrm{E}}\mathrm{E}$, $\overline{\mathrm{T}}_2\mathrm{T}_2$)	2	4, 9
E_4 ($\overline{\mathrm{A}}_2\mathrm{T}_2$, $\overline{\mathrm{E}}\mathrm{T}_2$, $\overline{\mathrm{T}}_2\mathrm{A}_2$, $\overline{\mathrm{T}}_2\mathrm{E}$)	0	15, 6, 3, 6
E_5 ($\overline{\mathrm{T}}_1\mathrm{T}_2$, $\overline{\mathrm{T}}_2\mathrm{T}_1$)	–2	9, 9
E_6 ($\overline{\mathrm{T}}_1\mathrm{T}_1$)	$1-c$	9
E_7 ($\overline{\mathrm{A}}_1\mathrm{E}$, $\overline{\mathrm{E}}\mathrm{A}_1$)	–4	10, 2
(3) C3v	$c=\sqrt{17}$	
E_1 ($\overline{\mathrm{A}}_1\mathrm{A}_1$)	3	5
E_2 ($\overline{\mathrm{T}}_1\mathrm{T}_1$)	$(1+c)/2$	9
E_3 ($\overline{\mathrm{T}}_2\mathrm{E}$, $\overline{\mathrm{E}}\mathrm{T}_2$)	2	6, 6
E_4 ($\overline{\mathrm{T}}_2\mathrm{T}_2$)	$(-1+c)/2$	9
E_5 ($\overline{\mathrm{A}}_2\mathrm{T}_1$, $\overline{\mathrm{T}}_1\mathrm{A}_2$)	1	15, 3
E_6 ($\overline{\mathrm{T}}_1\mathrm{T}_2$, $\overline{\mathrm{T}}_2\mathrm{T}_1$, $\overline{\mathrm{E}}\mathrm{E}$)	0	9, 9, 4
E_7 ($\overline{\mathrm{A}}_1\mathrm{T}_2$, $\overline{\mathrm{T}}_2\mathrm{A}_1$)	–1	15, 3
E_8 ($\overline{\mathrm{T}}_1\mathrm{T}_1$)	$(1-c)/2$	9
E_9 ($\overline{\mathrm{T}}_1\mathrm{E}$, $\overline{\mathrm{E}}\mathrm{T}_1$)	–2	6, 6
E_{10} ($\overline{\mathrm{T}}_2\mathrm{T}_2$)	$(-1-c)/2$	9
E_{11} ($\overline{\mathrm{A}}_1\mathrm{A}_1$)	–3	5

Now, the energy levels are reduced in each type so that the difference between the lowest two levels is the absolute value of *a*. From four types of tunneling energy levels, we may produce the following thermodynamic quantities. First, the internal energy is expressed as the value averaged by Boltzmann factor as follows:

$$U=<E>=\frac{\sum_{\mathrm{i}} E_{\mathrm{i}}\exp\left(-\frac{E_{\mathrm{i}}}{kT}\right)}{\mathrm{Z}} \qquad (2)$$

where partition function is given by $Z=\sum_{\mathrm{i}}\exp(-E_{\mathrm{i}}/kT)$. Next, heat capacity is formulated as

$$\frac{C_{\mathrm{v}}}{k}=\frac{1}{(kT)^2}(<E^2>-<E>^2) \qquad (3)$$

Here, E^2 is averaged in the same manner as in Eq. (2).

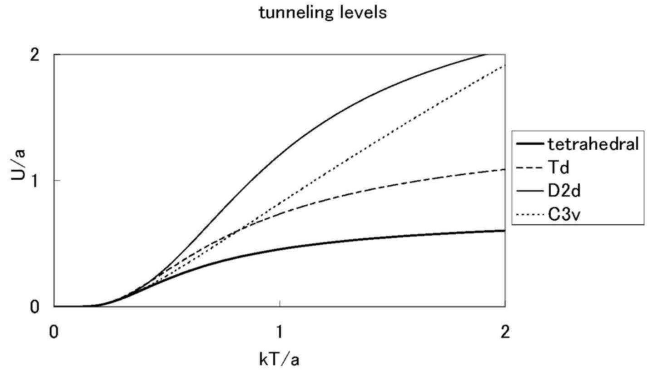

Fig. 1 Temperature dependence of internal energy in four types of tunneling system. The unit of energy *U* or *kT* is *a*-value in matrix element

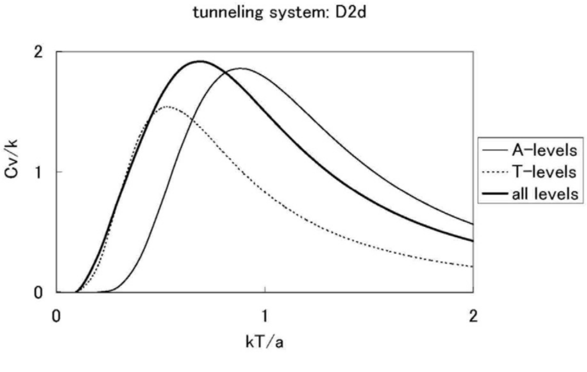

Fig. 2 Temperature dependence of heat capacity in the tunneling system with D2d orientational symmetry. The curves for A-levels, T-levels, and all levels are separately depicted

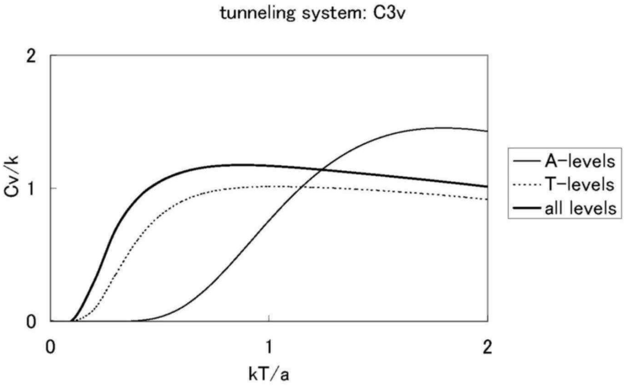

Fig. 3 Temperature dependence of heat capacity in the tunneling system with C3v orientational symmetry. The curves for A-levels, T-levels, and all levels are separately depicted

In Fig. 1, the energy is shown in four types. The curve in C3v goes up most highly as expected from the level structure. The increasing of others resembles closely. Thus, we plot the heat capacity in only D2d and C3v as typical cases. In Fig. 2, we see the usual anomaly in heat capacity in D2d. The contributions from A-levels and T-levels are also depicted. Each one has the similar shape. In contrast, C3v type has the quite different behavior in two components: A-levels and T-levels as shown in Fig. 3. By T-levels, a little odd change appears.

In short, it is revealed experimentally that C3v type is most suitable in this system [1]. To investigate the serial shift [3] of the energy in the various AX lattices, we need to introduce the new kind of symmetry due to the mismatch in ionic size. Construction of such a model is in progress.

References

1 A. Inaba, H. Chihara, J. A. Morrison, H. Blank, A. Heidemann and J. Tomkinson, J. Phys. Soc. Jpn., 59 (1990) 522.
2 Y. Ozaki, J. Phys. Soc. Jpn., 56 (1987) 1017.
3 R. Mukhopadhyay, B. A. Dasannacharya, J. Tomkinson, C. J. Carlile and J. Gilchrist, J. Chem. Soc. Faraday Trans., 90 (1994) 1149.