Characterization of Cu^{2+} Impurity Ion in K$_2$SnCl$_6$:Cu Single Crystal

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K$_2$SnCl$_6$ single crystals doped with Cu were grown by the evaporation of saturated solution. The electron magnetic resonance (EMR) of the Cu^{2+} ion in the crystal has been investigated by using an X-band spectrometer. The rotation pattern in the crystallographic plane together with spin Hamiltonian parameters of Cu^{2+} ion in K$_2$SnCl$_6$:Cu single crystal shows that the local site symmetry of the Cu^{2+} ion is cubic at room temperature. The calculated spectroscopic splitting factor g of Cu^{2+} impurity ion is 2.1908($\pm$0.0007). The hyperfine constants of Cu^{2+} impurity ion due to the ^{63}Cu and ^{65}Cu isotopes in K$_2$SnCl$_6$:Cu crystal are 0.83($\pm$0.01)$\times 10^{-4}$ cm^{-1} and 0.89($\pm$0.01)$\times 10^{-4}$ cm^{-1}, respectively. It turns out that the Cu^{2+} ion substitutes for the K$^+$ ion without any nearby charge compensation.

Keywords : K$_2$SnCl$_6$ single crystal, Cu^{2+} EMR, local site symmetry, substitutional site

1. Introduction

K$_2$SnCl$_6$ is the prototype of the family of hexahalogeno-metallates of the general type A$_2$BX$_6$ which crystallizes at room temperature in the cubic anti-fluorite structure with space group Fm3m [1]. The bonding between A$^+$ and BX$_6$$^{2-}$ octahedron is ionic and within the BX$_6$ octahedron covalent bonding dominates between B metals and X halogens. The K$^+$ ion cages occupied by the BX$_6$$^{2-}$ octahedra per unit cell in the hexahalogenometallates are alternately half occupied.

The electron configurations of the B^{4+} metal ions decide the magnetic structure of the compounds and also significantly influence the mechanism of the metal-ligand binding in the BX$_6$ octahedron. The investigations of the magnetic properties [2-4] and the bonding mechanisms [5, 6] of the single crystal were the essential theoretical and experimental parts of research. The results of the thermal and spectral measurements [7] and the study of the lattice dynamics have provided important information on the phase transitions mechanism and the lattice dynamics.

The mixed crystals of these hexahalogenometallates compounds have been investigated thoroughly especially with NQR and Raman scattering [8-10]. However, there are many difficulties in understanding the properties of the local structure in detail, particularly, in the temperature region around the structural phase transitions as well as in the intermediate phase that is in the narrow temperature region between the high- and low-temperature phases. Around the phase transition region, the dynamic and static properties of the lattice vary abruptly with temperature. Complex phenomena also come out through the overlap of many different effects of the lattice dynamics. The phase transition of K$_2$SnCl$_6$ has been investigated in detail [11, 12].

Electron magnetic resonance (EMR) gives information on the local structure and site location of point defects as well as impurity ions. In these study, EMR spectra of Cu^{2+} ion in K$_2$SnCl$_6$:Cu single crystal obtained at an X-band are analyzed in terms of the effective spin Hamiltonian with the spin S = 1/2. The local site symmetry as well as EMR parameters of Cu^{2+} impurity ion is determined. The substitutional site of the Cu^{2+} ion is also discussed by considering the ionic size, charge state, and microscopic site symmetry.

2. Crystal Structure and Experimental Aspects

The K$_2$SnCl$_6$ crystallize in the cubic with space group O_h^5/Fm3m consisting of non-connected SnCl$_6$-octahedra on a face centered cubic (fcc) lattice and K atoms on a primitive cubic lattice with half the lattice constant at

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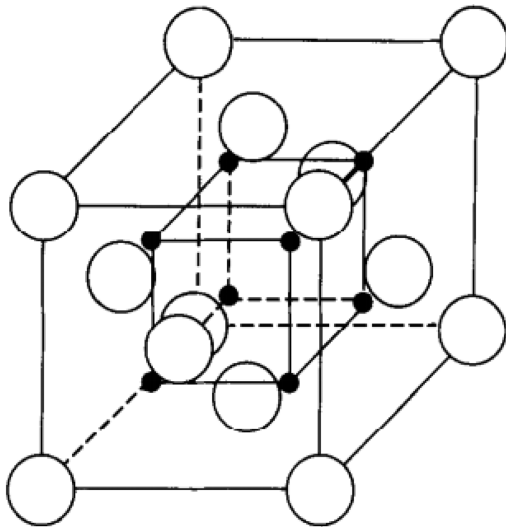Fax: +82-43-229-8498, e-mail: thyeom@cju.ac.kr

Fig. 1. Unit cell of cubic K_2SnCl_6 single crystal. The black circles denotes the K^+ cation and the large open circles the octahedral $(SnCl_6)^{2-}$ anion.
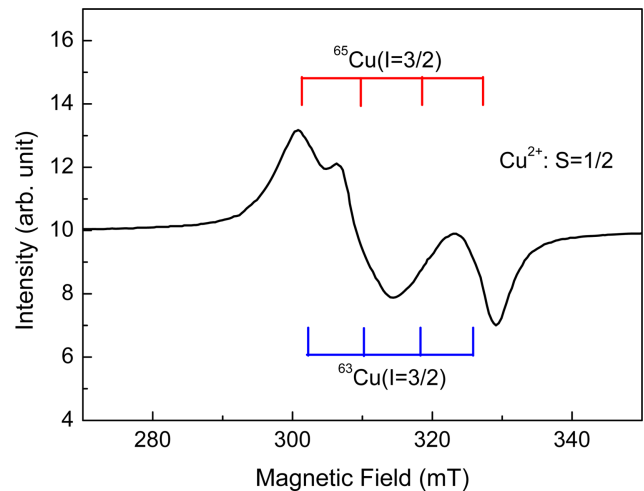

Fig. 2. (Color online) Typical EMR spectra of Cu^{2+} ion in the K_2SnCl_6:Cu single crystal at room temperature. The resonance spectra consist of isolated Cu^{2+} EMR center with two sets of hyperfine structures due to the ^{63}Cu and ^{65}Cu isotopes and clustered Cu^{2+} EMR center.

room temperature [13]. The unit cell, i.e. primitive unit cell has four molecules with nine atoms per molecule (two K, one Sn, and six Cl atoms) as shown in Fig. 1. The basis consists of a $(SnCl_6)^{2-}$ complex ion and two K^+ ions.

The crystal structure is an fcc with lattice constant $a = 0.9986$ nm at 280 °C. The bond lengths between atoms are Cl-Sn = 0.24106 nm, Cl-K = 0.35301 nm, Cl-Cl^n = 0.34091 nm, Cl-Cl^{nn} = 0.36491 nm at room temperature. The two phase transition temperatures at $T_{c1} = 260.5$ K and at $T_{c2} = 255$ K of K_2SnCl_6 are found by X-ray neutron diffraction with single crystals and powders [14]. The crystal structure of high temperature phase above T_{c1} is cubic (O_h^5). On cooling the crystal undergoes two successive phase transitions into an orthorhombic (D_{2h}^2) above T_{c2} and a monoclinic phase (C_{2h}^5) below T_{c2}.

The host crystal K_2SnCl_6 doped with the Cu^{2+} ion was grown by the vaporization of saturated solution. Potassium chloride (KCl) was melted in distilled water with 0.1 n HCl to yield saturated aqueous solution. The solution was then added to hydrogen hexachlorostannate (H_2SnCl_6) stoichiometrically to precipitate the powder of potassium hexachlorostannate (K_2SnCl_6).

The color of the powder obtained was snow-white. The powder was dissolved in distilled water and evaporated slowly to obtain single crystal. The K_2SnCl_6 single crystal was grown up in 0.5-5 mm after a few days. The host crystal K_2SnCl_6 is doped with Cu^{2+} (0.9 mol%).

We used an X-band JEOL (JES-RE2X) EMR spectrometer to get the Cu^{2+} EMR spectra in K_2SnCl_6 single crystal. The rotation patterns of the Cu^{2+} resonance fields

in the crystallographic planes were obtained at microwave frequency of 9.446 GHz. Only one set of resonance line was measured for Cu^{2+} in K_2SnCl_6:Cu single crystal. This EMR result agrees with the NQR frequency with a single line above $T \geq T_{c1}$ [15, 16].

Figure 2 shows a typical EMR spectra of Cu^{2+} impurity ion in K_2SnCl_6:Cu single crystal at room temperature. The fine structure of Cu^{2+} ion consists of only one resonance line because the effective spin S of the ion is 1/2. The fine structure is split into four lines each by the hyperfine interaction of ^{63}Cu (I = 3/2, 69.17 % abundance) and ^{65}Cu (I = 3/2, 30.83 % abundance) nuclei, respectively. The resonance spectra in Fig. 2 discussed later consist of isolated Cu^{2+} EMR center with two sets of hyperfine structures (8 lines) due to the ^{63}Cu and ^{65}Cu isotopes as well as clustered Cu^{2+} EMR center. We could not find any angular variation of electron magnetic resonance spectra for Cu^{2+} ion on the crystallographic aa-plane. This indicates that the local site symmetry of the Cu^{2+} ion K_2SnCl_6:Cu single crystal is cubic. From the rotation pattern, EMR parameters of the Cu^{2+} ion were determined.

3. Effective Spin Hamiltonian and Analysis

The Cu^{2+} ion has the electron configuration $3d^9$ and is a D-state ion characterized by $S = 1/2$ and the ground multiplet $^2D_{5/2}$. The hyperfine structure (zero field splitting) results from the interaction between the nuclear spins of ^{63}Cu and ^{65}Cu isotopes and their electronic spin. The

experimental resonance fields can be analyzed with an effective spin Hamiltonian [17, 18]:

$$H = H_Z + H_{hyp} = \mu_B \boldsymbol{B \cdot g \cdot S} + \boldsymbol{S \cdot A \cdot S}, \qquad (1)$$

where the terms H_Z are the Zeeman interaction and H_{hyp} the hyperfine interaction. μ_B is the Bohr magneton, $\boldsymbol{B}$ is the applied magnetic field, $\boldsymbol{g}$ is the spectroscopic splitting tensor, $\boldsymbol{S}$ is the electron spin, and $\boldsymbol{A}$ is the hyperfine tensor.

Magnetic resonance lines due to the hyperfine structure of Cu²⁺ in K₂SnCl₆ recorded in the crystallographic planes are used for calculating the spectroscopic splitting parameter g and the hyperfine constant A. The calculated g value of the isolated Cu²⁺ impurity ions is 2.1908(±0.0007) as shown in Table 1, where spectroscopic splitting parameter g is isotropic. The impurities with no neighboring Cu²⁺ impurity ions within the range of interaction are denoted as isolated Cu²⁺ ions.

The well-resolved resonance spectra arise from the magnetically diluted Cu²⁺ impurity ions (isolated Cu²⁺ EMR center) in the host lattice generally. However, the eight-line spectra were not resolved well in our K₂SnCl₆:Cu crystal doped with 0.9 mol% Cu concentrations as shown in Fig. 2. At 0.9 mol% Cu concentrations, the intensity of hyperfine structure of isolated Cu²⁺ impurity ions is very weak and broad signal becomes dominant. These broad-line spectra in Fig. 2 can be explained by a new Cu center (clustered Cu²⁺ EMR center) arising from the higher Cu concentrations. The broad resonance line due to clustered Cu impurity ions is strongly influenced by their Cu magnetic moments between clustered Cu ions.

The observed hyperfine resonance lines of Cu²⁺ impurity ion in K₂SnCl₆:Cu crystal are very weak, but their presence is indicated clearly. Two sets of hyperfine lines due to the isotopes ⁶³Cu ($I = 3/2$) and ⁶⁵Cu ($I = 3/2$) are indicated by the four red-colored bars and by the four blue-colored bars in Fig. 2, respectively. The last term in the Hamiltonian eq. (1) represents the hyperfine interaction. Since the hyperfine interaction term is known to be much smaller than the Zeeman term in Eq. (1), it is sufficient to regard it as the first-order perturbation to the Zeeman term. The calculated hyperfine constants of Cu²⁺ impurity ion due to the ⁶³Cu and ⁶⁵Cu isotopes in K₂SnCl₆:Cu crystal are $A^{63} = 0.83$ (±0.01)×10⁻⁴ cm⁻¹ and $A^{65} = 0.89$ (±0.01)×10⁻⁴ cm⁻¹ as shown in Table 1, respectively. The hyperfine constants are isotropic within the experimental accuracy both ⁶³Cu and ⁶⁵Cu nuclei in K₂SnCl₆ crystal. The ratio $A(^{65}Cu)/A(^{63}Cu)$ for Cu²⁺ ion in K₂SnCl₆ is 1.0723. This value (1.0723) is similar to the ratio of magnetic moments $\mu(^{65}Cu)/\mu(^{63}Cu) = 1.0712$ [19], as it ought to be.

To identify the substitutional site location of the Cu²⁺ ion in the K₂SnCl₆ single crystal, several points are considered as follows. First, the ionic sizes of Cu²⁺ and host ions in the K₂SnCl₆ crystal are compared in Table 2. The ionic radius of the Cu²⁺ ion is about 0.071-0.087 nm depending on the coordination number. It is reasonable to assume that Cu²⁺ ion occupies the K⁺ ion instead of the Sn⁴⁺ because the ionic radius of the K⁺ ion (0.151-0.152 nm) is larger than that of the Sn⁴⁺ ion (0.069-0.083 nm). On top of that, the charge state of the Cu²⁺ ion is closer to the K⁺ ion rather than that of the Sn⁴⁺ ion. Therefore, the Cu²⁺ ion can substitute for the K⁺ ion with remotely charge compensation. Suppose that Cu²⁺ ion resides at the Sn⁴⁺ site, which is unfavorable from the ion size, local distortion at the Sn⁴⁺ site would arise because the ionic radius of the Sn⁴⁺ is smaller than that of the Cu²⁺ ion. The cubic local site symmetry of the Cu²⁺ ion obtained from our EMR analysis favors the assumption that the Cu²⁺ ion occupies the K⁺ ion at the cubic symmetry. Therefore, it is reasonable to conclude that the Cu²⁺ ion replaces the K⁺ ion without local charge compensation at the nearby surroundings.

4. Results

K₂SnCl₆ single crystals doped with Cu²⁺ ion were grown by the vaporization of saturated solution. The rotation

Table 1. The spectroscopic splitting parameter g and hyperfine constants A of the isolated Cu²⁺ impurity ion in a K₂SnCl₆:Cu single crystal. The unit of A is 10⁻⁴ cm⁻¹.

g-factor	$A(^{63}Cu)$	$A(^{65}Cu)$	$A(^{65}Cu) / A(^{63}Cu)$	$\mu(^{65}Cu) / \mu(^{63}Cu)$
2.1908(±0.0007)	0.83(±0.01)	0.89(±0.01)	1.0723	1.0712

Table 2. The ionic radii of the Cu²⁺ ion and the host cations in the K₂SnCl₆ single crystal.

ions	Cu²⁺		K⁺		Sn⁴⁺	
Coord. Number	4	6	4	6	4	6
radii (nm)	0.071	0.087	0.151	0.152	0.069	0.083

patterns of Cu^{2+} ion are observed on the crystallographic *aa*-plane at room temperature. The hyperfine constants A as well as the spectroscopic splitting factor g of the Cu^{2+} EMR center have been determined with the effective spin Hamiltonian. The isotropic g and A values together with rotational patterns of Cu^{2+} impurity ion show that the Cu^{2+} ion reside at the cubic symmetry site. This EMR study enables us to conclude that the local site symmetry of the Cu^{2+} center in K_2SnCl_6 single crystal is cubic. It is proposed that the Cu^{2+} ion in the crystal substitutes for the K^+ ion without local charge compensation at surroundings close by.

Acknowledgement

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