Superionic Conductors and Anharmonic Lattice Vibration

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Important role played by anharmonic lattice vibration in superionic conductors is pointed out. As an example,anisotropic and large anharmonic vibration of Cu ion in α -CuI crystal is discussed. A mechanism of the sublattice melting is proposed in which cooperative interaction between Cu and I ions leads to an instability in Cu sublattice.

§1 Introduction

Superionic conductors are special ionic systems: Group of ions of one kind constitute a rigid regular lattice, through which another group of ions perform fast diffusion, giving rise to a high ionic conductivity. This means that at least one part of crytal, namely the crystalline order of one sublattice, is destroyed in conducting phase (sub-lattice melting), and therefore it is expected that before the system undergoes a transition to superionic conducting phase, a remarkable increase in the amplitude of the anharmonic vibration should be realized as a precursor phenomenon, because the concerned sublattice is fated to melt and ions in it would execute violent anharmonic motions to assist break down of the sublattice. There is a few experimental evidence for that this is indeed the case.

As to the origin of the large anharmonicity, a conspicuous fact should be noticed: In most $3-d$ superionic conductors, the mobile ion often occupies a non-centro symmetric position in the crystal lattice. For instance Cu^+ ion in CuI and CuCl is located at a center of tetrahedron formed by four neighbouring anions as depicted in Fig. 1, and similarly Ag^+ ion in α -AgI at one of centers of distorted tetrahedra as shown in Fig. 2. The characteristic feature of such low symmetry sites lies in that the anharmonic part in the effective local potential for the occupying ions starts with the third order term instead of usual fourth order term as in cubic system. To be more specific, the potential energy of a Cu^+ ion as a function of displacements from the center in Fig. 1 reads as
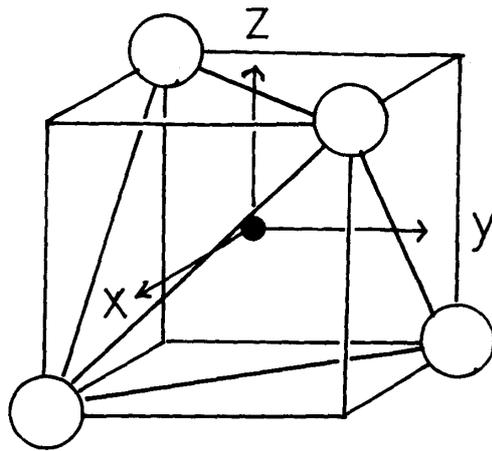
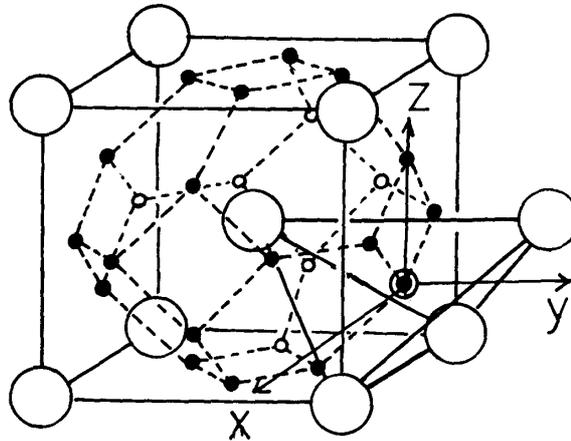Fig. 1 Non-centro-symmetric position occupied by a Cu^+ ion in α-CuI crystal.

Fig. 2 The sites occupied by Ag^+ ion in α-AgI crystal.

$$V = V_0 + \frac{1}{2}a(x^2 + y^2 + z^2) + b\ xyz + \frac{1}{4}c(x^4 + y^4 + z^4) + \ldots \tag{1}$$

and similarly for Ag^+ ion in Fig. 2 as

$$V = V_0 + \frac{1}{2}a(x^2 + y^2) + \frac{1}{2}a'\ z^2 + \frac{1}{2}b(x^2 z - y^2 z) + \ldots \tag{2}$$

The inportance of the third order term of (1) in interpreting the observed facts of structural phase transition in CuI was first pointed out by the present author as early as in 1952, and by making detailed calculation it was shown that the entropy changes in γ-β and β-α phase transitions and observed large Debye-Waller factor can be quantitatively well explained.[1] A similar calculation based on the potential (2) for AgI was also carried out by Hoshino et al [2] and the results were successfully compared with their experimental data of X-ray scattering.

The aim of this paper is to generalize our previous theory so as to determine both the anharmonic potential and amplitude of the anharmonic vibration for Cu ion in CuI self-consistently as functions of temperature and to propose a possible mechanism of sublattice melting.

§2 Self-consistent Einstein Model

To deal with large anharmonic vibration of ion around a non-centro symmetric site, the most simple and effective approach will be to adopt the self-consistent phonon theory (SCPT). As one simplified version of SCPT, we formulate in this section a variation principle which leads to the self-consistent Einstein model.[3]

Consider for example a Cu ion in α-CuI crystal which is surrounded by four I ions tetrahedrally. Let us assume an anharmonic potential for the Cu ion in a form:

$$\phi(x,y,z)=\frac{1}{2}a(x^2+y^2+z^2)+b\ xyz+\frac{1}{4}c(x^4+y^4+z^4)+\ldots \tag{3}$$

where a, b and c are parameters to be determined later self-consistently. In the high temperature approximation, where classical statistical mechanics may be used, the probability distribution of Cu ion displacement is described by a density function

$$p(x,y,z)=\exp[-\phi(x,y,z)/k_B T]/Z \tag{4}$$

with

$$Z=\int\int\int\exp[-\phi(x,y,z)/k_B T]dxdydz. \tag{5}$$

Let $v(r)$ be the relevant potential acting between a Cu ion and I ion separated by the distance r. The potential energy of a Cu ion is then a sum of four terms $v(\mathbf{R}_i-\mathbf{r})$, i = 1, 2, 3, 4, contributed from the four neighbouring I ions located at $\mathbf{R}_1 = (d,d,d)$, $\mathbf{R}_2 = (-d,-d,d)$, $\mathbf{R}_3 = (d,-d,-d)$, and $\mathbf{R}_4 = (-d,d,-d)$ respectively (see Fig. 1). Thus we denote the potential energy of a Cu ion as

$$V(x,y,z)=\sum_{i=1}^{4}v(\mathbf{R}_i-\mathbf{r}). \tag{6}$$

Now a variation principle to determine the anharmonic motion of the Cu ion can be formulated in the following way: By making use of a notation

$$<\ldots\ldots>=\int\int\int dxdydz\ p(x,y,z)\ldots\ldots \tag{7}$$

we give a trial free energy per Cu ion in the form:

$$f(a,b,c)=<V(x,y,z)>+k_B T<\ln p(x,y,z)>. \tag{8}$$

We require that the free energy $f(a,b,c)$ should be minimum with respect to the variation of the parameters a,b and c:

$$\partial f(a,b,c)/\partial a=\partial f(a,b,c)/\partial b=\partial f(a,b,c)/\partial c=0. \tag{9}$$

This gives us a set of coupled equations to determine the parameters a, b and c and hence the probabilty distributuion $p(x,y,z)$ self-consistently. It turns out that the equations take on very simple forms:

$$a = \langle \partial^2 V(x,y,z) / \partial x^2 \rangle \equiv F_a(a,b,c) \tag{10a}$$

$$b = \langle \partial^3 V(x,y,z) / \partial x \partial y \partial z \rangle \equiv F_b(a,b,c) \tag{10b}$$

$$c = (1/6) \langle \partial^4 V(x,y,z) / \partial x^4 \rangle \equiv F_c(a,b,c). \tag{10c}$$

The proof of the statements (10a−c) is based on the following two facts that the characteristic function of the probability distribution p(x,y,z) can be defined as

$$\langle \exp(i k.r) \rangle = \exp[-(k^2/6) \langle r^2 \rangle_c - i k_1 k_2 k_3 \langle xyz \rangle_c$$
$$+ (1/4!)(k_1^4 + k_2^4 + k_3^4) \langle x^4 \rangle_c + . .] \tag{11}$$

and the cumulant averages in (11), $\langle r^2 \rangle_c$, $\langle xyz \rangle_c$ and $\langle x^4 \rangle_c$ are linearly independent functions of a, b and c. To be more precise, we assume that V(r) may be expressed as

$$\langle V(r) \rangle = \int V(k) \langle \exp(-i k.r) \rangle dk \tag{12}$$

and put this in (8) and use the formula (11). Then we find that $\langle V(r) \rangle$ is a function of a, b and c only through $\langle r^2 \rangle_c$, $\langle xyz \rangle_c$ and $\langle x^4 \rangle_c$. Therefore if we perform the variation of f(a,b,c) with respect to a,b and c, we finally obtain a set of coupled equations of the following forms:

$$C_1 \partial \langle r^2 \rangle_c / \partial a + C_2 \partial \langle xyz \rangle_c / \partial a + C_3 \partial \langle x^4 \rangle_c / \partial a = 0$$

$$C_1 \partial \langle r^2 \rangle_c / \partial b + C_2 \partial \langle xyz \rangle_c / \partial c + C_3 \partial \langle x^4 \rangle_c / \partial c = 0$$

$$C_1 \partial \langle r^2 \rangle_c / \partial c + C_2 \partial \langle xyz \rangle_c / \partial c + C_3 \partial \langle x^4 \rangle_c / \partial c = 0 \tag{13}$$

with

$$C_1 = -\frac{1}{2}a - (1/6) \int k^2 V(k) \langle \exp(i \cdot k.r) \rangle dk$$

$$C_2 = -b - i \int k_1 k_2 k_3 V(k) \langle \exp(i \cdot k.r) \rangle dk$$

$$C_3 = -(3/4)c + (1/8) \int k_1^4 V(k) \langle \exp(i \cdot kr) \rangle dk. \tag{14}$$

Because $\langle r^2 \rangle_c$, $\langle xyz \rangle_c$ and $\langle x^4 \rangle_c$ are linearly independent functions of a,b and c, the associated Jacobian cannot vanish:

$$\begin{vmatrix} \partial \langle r^2 \rangle_c / \partial a & \partial \langle xyz \rangle_c / \partial a & \partial \langle x^4 \rangle_c / \partial a .. \\ \partial \langle r^2 \rangle_c / \partial b & \partial \langle xyz \rangle_c / \partial b & \partial \langle x^4 \rangle_c / \partial b .. \\ \partial \langle r^2 \rangle_c / \partial c & \partial \langle xyz \rangle_c / \partial c & \partial \langle x^4 \rangle_c / \partial c .. \end{vmatrix} \neq 0 . \tag{15}$$

Thus it follows from (13) and (15) that

$$C_1 = C_2 = C_3 = 0. \tag{16}$$

It is an easy task to check that (16) is equivalent to (10 a—c).

§3 Application to Sublattice Melting

The main result (10 a—c) derived in §2 has very clear physical meaning. It says that the initially assumed potential $\phi(x,y,z)$ should be equal to $<V(r)>$ which is the actual potential averaged over anharmonic motion under the assumed potential ϕ. In another word the formula (3) should be an expansion form of $<V(x,y,z)>$ around the origin. Now we shall apply our general formulation to a case of specific potential $v(r)$. Although there are debates on the interatomic(ionic) potentials which play essential role in superionic conductors, we focus our attention on the precursor behaviour of Cu ion and regard repulsive force between Cu^+ ion and four neighbouring I^- ions most important. For simplicity we shall take

$$v(r) = v_0 \exp(-s \mid r \mid) \tag{17}$$

and calculate

$$<V(r)> = \sum_{i=1}^{4} v_0 <\exp(-s \mid R_i - r \mid)> \tag{18}$$

where with minor modification the expansion (11) may be utilized to obtain

$$<V(r)> = (\sum_{i=1}^{4} v_0 \exp(-s \mid R_i - r \mid)) \cdot \exp(\frac{s^3}{3\sqrt{3}}<xyz>_c) \tag{19}$$

Since we are mainly interested in the third order anharmonicity, the effects of $<r^2>_c$ or $<x^4>_c$ are renormalized into the prefactor in (19). Thus eventually we arrive at an equatioan (10b) for b in a form

$$b = F_b(a,b,c) = b_0 \exp(\frac{s^3}{3\sqrt{3}}<xyz>_c). \tag{20}$$

As already noticed, $<xyz>_c$ is a function of b, and the solution of eq. (20) can be attained by a graphical method as schematically shown in Fig. 3. It turns out that we have no solution above a certain temperature T_c, indicating that a local minimum of the free energy disappears and Cu ion becomes unstable at the assumed tetrahedral position. This suggests the occurrence of the sublattice melting. The actual sublattice melting would, however, take place at a certain temperature T_m lower than T_c. This can be seen from the following observation. The assumed potential (3) has finite barriers along the direction with $xyz < 0$. The height of the barrier $\phi_c(b)$ is mainly determined by the value of b, and we have to impose a condition that
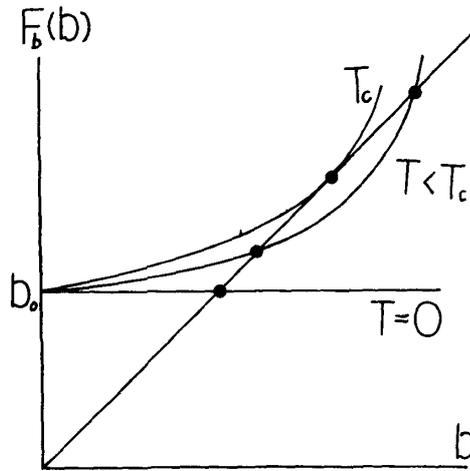
Fig. 3 Graphical representation of the equation (20) with fixed a and c.

$$k_B T < \phi_c(b) \tag{21}$$

in order that our theory should be consistent. Thus value of b is bounded for each temperature at, say, $b_c(T)$ by the condition (21). Therefore at a certain temperature T_m the free energy will become equal at both the minimum point b_m and boundary point $b_c(T_m)$. In essence, the anharmonic potential (3) causes a large anisotropic vibration of Cu ion, which in turn produces more anisotropic effective potential, leading to the reduction in the height of the potential barriers along the special directions and finally yielding an instability of the original position of the Cu ion accompanied by an ionic migration through the lowered potential barriers.

References

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