

Roles of phonon amplitude and low-energy optical phonons on superionic conduction

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From a simple equation of motion for a linear chain, the phonon amplitudes for mobile and cage ions are represented in terms of their ionic radius and atomic mass. Estimated values of the amplitude in superionic conductors are larger for the mobile ions than the cage ions. Based on this result, many binary and ternary ionic conductors are classified into superionic or normal-ionic conductors. The role of low-energy optical (LEO) phonon is to enhance the phonon amplitude and assist the jump of mobile ions. This is ascertained from the relationship between the frequency of the LEO phonon and the activation energy, which is similar to self-diffusion in bcc metals. [S0163-1829(97)05141-2]

I. INTRODUCTION

Only a certain number of compounds exhibits high-ionic conduction.^{1,2} For such compounds, Wakamura suggests the cause is a noninteger value of the effective chemical valence Z_{eff} (Refs. 3 and 4) which is caused by the d electron at the outermost orbit as suggested from several relationships about the optical dielectric constant ϵ_{∞} , the Szegedi effective charge e_s^* , the short-range force potential, etc.⁴ Similar values of Z_{eff} are pointed out empirically by Lawaetz, who estimates the Z_{eff} for AgI and Cu halides from the relationship between the ratios of lattice constants for the a and c axes, c/a , and the $C/Z_{\text{eff}}(\hbar\omega_p)^2$ value, where C or ω_p represent the homopolar gap energy or plasma frequency.⁵ Tomoyose, Fukuchi, and Aniya presented theoretically noninteger values of Z_{eff} for AgI and Cu halides by taking into account the effect of d electrons.⁶

The d electron at the outermost orbit exhibits a considerable hybridization with the p electron at the top of the valence band in superionic conductors (SIC's).⁷⁻⁹ Although the hybridization does not arise in most of the high-ionic conductors (HIC's),^{10,11} an exception appears, for example, on AgF since it exhibits substantial hybridization near the top of the valence band.¹² Further, the Z_{eff} of isoelectronic SIC's and HIC's does not take clearly different values. For example, the Z_{eff} value of SIC AgI and CuX ($X=\text{Br},\text{I}$) take similar magnitudes to those of the isoelectronic compounds AgX ($X=\text{F},\text{Cl},\text{Br}$) and CuF, respectively.^{3-5,13,14}

Based on these results, we attempt to find a characteristic factor of the SIC. We now notice an optical phonon at low energy (LEO phonon) since the low energy is determined by interionic forces depending on the specific ionic and covalent properties of the SIC. Such a phonon does not seem to appear in HIC's. Further, the phonon damping of the LEO phonon takes a large value below the transition temperature T_c ,¹⁵⁻¹⁸ revealing strong coupling with the mobile ions as pointed out theoretically by Bunde,¹⁹ Pardee and Mahan,²⁰ etc.²¹ An example of such a phonon is the E_2 mode at 17 cm^{-1} in AgI,²² which exhibits an acousticlike property.²³ Although the importance of this mode is anticipated from the acoustic phonon in the self-diffusion of bcc metals,²⁴ the understanding of the LEO phonon in many SIC's is not enough.

To elucidate the relation between the LEO phonon and the conductive ion, we note the phonon amplitude and classify ionic conductors into SIC's or non-SIC's. It is achieved without requiring the knowledge of crystal structure. This classification is a guide for understanding the characteristic relation between the conductive property^{1,2} and crystal structures in SIC's and HIC's. Many superionic conductors are examined to find whether the mechanism is common over many SIC's or not.

In the following section, we describe the process leading to the vibration amplitudes for cations and anions based on a simple linear chain. Although such a process is simple, it gives an intuitive guide for systematic treatment over many binary and ternary compounds. In Sec. III, the process is achieved and the SIC is classified from the HIC. In Sec. IV, the importance of the LEO phonon is discussed with respect to the amplitude. Based on the correlation between the lowest frequency of the optical phonon at the zone center and the activation energy E_{ac} , the conductive ions assisted by the optical phonon is indicated. The effective role of the optical phonon is interpreted with respect to the phase of vibrational ions.²⁵ The obtained results are compared with the self-diffusion in bcc metal and the correspondence between the acoustic phonon in metal and the optical phonon in SIC's is suggested.

II. PHONON AMPLITUDES OF CATIONS AND ANIONS

We first attempt to estimate the vibrational amplitudes of mobile and cage ions below T_c using a point ion model in which a point ion has mass m , charge Z^*e , spring force f averaged over the constituent ions, and a restoring force proportional to the speed of the vibrational ion. The proportional constant, called the damping constant,²⁶ must take different values for the cation and anion because of their different polarizabilities due to the deformation of the outermost orbit in HIC's. Therefore the effect of polarization on the vibrational amplitude must be dependent on the kind of ions. In Ag- (or Cu-) halide SIC, this difference will be extremely large because the large polarization of the Ag (or Cu) ion results from a soft electron cloud shell that depends on a strong contribution of the $4d$ (or $3d$) electrons of the Ag (or

Cu) ion with the $4p$ electrons of the halide ion at the top of the valence band.⁷⁻⁹

The equation of motion for the A ion is then written as²⁶

$$m_A \ddot{u}_A - \gamma_A m_A \dot{u}_A + f_A u_A = Z^* e E, \quad (1)$$

where m_A , u_A , γ_A , and f_A represent the atomic mass, displacement, damping constant, and spring force of the A ions, respectively. $Z^* e$ is the ionic charge, which may take approximately equal values for the cation and anion under the charge neutrality condition, and E is the electric field around the A ion. Under the time dependencies $u_A = X_A \exp(-i\omega t)$ and $E = E_V \exp(-i\omega t)$, Eq. (1) becomes

$$-m_A \omega^2 X_A + i \gamma_A \omega m_A X_A + f_A X_A = Z^* e E_V. \quad (2)$$

At the resonance state, we assume the value of ω to be $\omega_{TO} [(f_A/m_A)^{1/2}]$, then, Eq. (2) becomes $iX_A = Z^* e E_V / m_A \omega_{TO} \gamma_A$ and the absolute value of X_A , u_{A0} , is obtained by employing the absolute value of E_V , E_0 , as

$$u_{A0} = (Z^* e / m_A \omega_{TO} \gamma_A) E_0. \quad (3)$$

A nonzero value of $Z^* e$, implying an optical phonon, gives a finite value for the vibration amplitude.

From Eq. (3), we can obtain a subtracted value for the amplitudes of the mobile ion A and cage ion X as

$$\begin{aligned} (u_{A0} - u_{X0}) &= (Z^* e E_0 / \omega_{TO}) [(1/\gamma_A m_A) - (1/\gamma_X m_X)] \\ &= (Z^* e E_0 / \omega_{TO}) [(\gamma_X m_X - \gamma_A m_A) / \gamma_A \gamma_X m_A m_X] \\ &= Z^* e E_0 R_G \omega_{TO}, \end{aligned} \quad (4)$$

where R_G represents the value $[(\gamma_X m_X - \gamma_A m_A) / \gamma_A \gamma_X m_A m_X]$.

To describe the main features of the $(u_{A0} - u_{X0})$ in Eq. (4), we consider only the R_G value. Further, in order to estimate the numerical value of R_G without requiring the knowledge of crystal structure, we assume that the damping constants, γ_A and γ_X , are roughly proportional to the ionic radius with a proportional constant b as

$$\gamma_A = b r_A$$

and

$$\gamma_X = b r_X. \quad (5)$$

Under constant temperature, this assumption seems to be reasonable as the phonon damping constant generally takes a larger value for compounds with a heavier atomic mass if they are isoelectronic compounds.^{27,28} Different values for γ_A and γ_X have been reported for the observed values in a layered superionic conductor AgCrS_2 .^{29,30} The damping constant of the phonon mode shows a rapid decrease above T_c when the mode is constructed from only cage ion vibration, however, increases rapidly for the mode involving mobile ion vibration.³⁰ These facts indicate that the phonon band showing rapid broadening is closely related to the movable ions, while that relating to cage ions is the opposite, showing rapid narrowing. This tendency is held below T_c because the large value of phonon damping generally appears there.

Using Eq. (5), the R_G value in Eq. (4) is represented as

$$R_G = (r_X m_X - r_A m_A) / r_A r_X m_A m_X b. \quad (6)$$

From Eqs. (4) and (6), a positive value of R_G reveals that the mobile ion amplitude is larger than that for the cage ions, while a negative value reveals the opposite.

III. ESTIMATION OF PHONON AMPLITUDES IN SUPERIONIC CONDUCTORS

We now estimate the R_G values for $b=1.0$ in Eq. (6) for binary and ternary SIC's which take a noninteger value of the chemical valence.^{3,4} The R_G values of isoelectronic compounds are also listed in Table I and plotted in Fig. 1. The values of the ionic radii are taken from the data by Pauling (collected by Chandra),² although Goldshmit's data² give almost the same results.

A. Binary compounds

In Ag- and Cu-ion conductors, the cation A is movable and the R_G values for $(u_{A0} - u_{X0})$ are listed together with the T_c value in Table I.^{1,2,31} In alkaline-earth halides, the halide ion X is the mobile ion, and the R_G values for $(u_{X0} - u_{A0})$ are listed. The R_G values for SIC's and non-SIC's are shown by an open circle and a triangle in Fig. 1, respectively. Except for a few compounds, clear regularity is found, that is, SIC's and non-SIC's take positive and negative values, respectively. Based on this regularity, we classify AgI, CuCl, CuBr, and CaF_2 as SIC's and AgCl and CuF as non-SIC's. In particular, we can obtain a clear classification for the isoelectronic binary compounds, for example, CaF_2 and CaCl_2 , CuBr and CuF, and for Cu_2S and Cu_2O , in which the former is SIC and the latter is non-SIC. These classifications agree with the experimental results.

We propose two conditions to be satisfied for SIC. The first is a noninteger value of Z_{eff} , as mentioned in Sec. I.³ The second is the amplitude of the mobile ion vibration for an optical phonon, which is larger than that of the cage ion. This nature is similar to that of thermal vibration reported already.^{25,32-35} Tomoyose derives the amplitudes of thermal vibration in AgI and CuX ($X=\text{Cl,Br,I}$) under quantum dielectric theory and estimates that the amplitude of the mobile ion is larger than that of the cage ion.³² The results are consistent with previously reported data.³³⁻³⁵ Dalba *et al.*²² and Buhner, Nicklow, and Brüesch²³ found that the amplitude of the Ag ion is larger than that of the I ion in AgI and a more rapid increase with rising temperature by neutron-scattering measurements. From this result, we may anticipate that the vibrational amplitude of the movable ion in the optical mode is larger than that of the cage ions in the high-temperature region.

For a few compounds in Table I, the regularity is not established. For example, SrBr_2 takes a small R_G value with a negative sign despite being a SIC, and BaBr_2 exhibits opposite behavior. For these irregularities, we consider the effect of the large polarizability of the Br ion, predicted from its ionic radius,³⁶ since Eq. (5) may give the irregularity, if the ionic radius of the Br ion is dependent on the kind of constituent cation.

Ag_2S is a SIC but takes a negative value of R_G . For this anomaly, the large quadrupole deformation of the Ag ions may be the cause since Cu_2S exhibits a smaller quadrupole deformation than that of Ag_2S and belongs to the regular

TABLE I. R_G values for $b=1.0$ in cubic and near cubic binary superionic conductors and their isoelectronic compounds. The data for T_c and ionic radii are from Samara (Ref. 31) and Chandra (Ref. 2), respectively. The phonon frequencies, taken from Buhner and Bill (Ref. 58) for Na_2S , and Brüesch and Wullschlegel (Ref. 59) for Ag_2S , are indicated in parentheses. The dashes and spaces in the T_c column indicate non-SIC's and unknown, respectively.

Com. (ω_{ph}) (cm^{-1})	T_c (K)	R_G (1/g cm)	Com. (ω_{ph}) (cm^{-1})	T_c (K)	R_G (1/g cm)
CuF (-)	-	-1.32×10^{-30}	CaF ₂ (266)	1423	0.84×10^{-30}
CuCl(172)	673	0.06	CaCl ₂	-	-0.60
CuBr(141)	664	0.60	CaBr ₂	-	-1.14
CuI(128)	642	0.78	CaI ₂	-	-1.32
AgF(170)	-	-1.87	SrF ₂ (219)	1453	1.74
AgCl(106)	-	-0.48	SrCl ₂ (140)	990	0.36
AgBr(79)	-	0.06	SrBr ₂	918	-0.24
AgI(17)	419	0.24	SrI ₂	-	-0.42
AuCl	-	-0.72	BaF ₂ (189)	1238	1.99
AuBr	-	-0.18	BaCl ₂	1193	0.36
AuI	-	0.00	BaBr ₂	-	0.06
Ag ₂ O	-	-2.11	BaI ₂	-	-0.12
Ag ₂ S(35)	452	-0.58	PbF ₂ (106)	703	1.99
Ag ₂ Se	406	0.06	PbCl ₂	763	1.50
Ag ₂ Te	423	0.24	PbBr ₂	-	0.00
Cu ₂ O	-	-1.56	PbI ₂	-	-0.12
Cu ₂ S	673	0.36	Na ₂ S(208)	1273	1.74
Cu ₂ Se	383	0.60	ThO ₂	-	2.29
Cu ₂ Te	600	0.78	UO ₂ (280)	2573	2.29
Au ₂ S	-	-0.80			
Au ₂ Se	-	-0.16			
Au ₂ Te	-	0.01			

pattern. Because of this, if the value of b in Eq. (5) depends on the kind of cage and mobile ions, the irregularity will disappear. Indeed, we can expect such a value of b because of a more intense polarizable Ag ion and a typical covalent S ion in Ag_2S .

Li halides take positive values of R_G but do not exhibit superionic conduction. Strong coupling of Li ions with the nearest-neighboring anions, resulting from its small ionic radius,³⁷ may be related to the cause of the irregularity since this coupling can change the value of b in Eq. (5).

B. Ternary compounds

To confirm the generality of the regularity in Fig. 1, we apply Eq. (6) to a ternary SIC. For the atomic mass and ionic radius of the cage ion, we employ averaged values with simplified forms $(m_A + m_B)/2$ and $(r_A + r_B)/2$, respectively. The R_G values are obtained under the same procedure as that for binary ionic conductors. The results are listed in Table II. Good regularity is shown except for Ag_3SBr and Ti_2ZnI_4 . From this result, we consider that Eq. (4) is justified within first approximation and it reveals that the ionic motion can be enhanced more effectively by the amplitude of mobile ions, being larger than that of cage ions. In Ti_2ZnI_4 , the R_G value is negative and ionic conductivity takes a low value, though the phase transition arises at 523 K.¹⁷ In Ag_3SBr , the effect of the large polarizability of the Br ion may appear again.

IV. DISCUSSION

In this section, we discuss the important role of the vibrational amplitude of the LEO phonons for realizing superionic conduction and show an empirical correlation between the lowest frequency of optical phonons and the E_{ac} value.

A. Role of frequency for enhancement of phonon amplitude

To consider the role of the optical phonon frequency, we suggest the mixed systems $\text{Ag}_x\text{Cu}_{1-x}\text{Br}$ (Ref. 38) or $\text{AgI}_{1-x}\text{Br}_x$, (Ref. 39) which exhibit superionic or nonsuperionic conduction at $x=0$ or $x=1$. Here the largest value of ionic conductivity σ appears in the intermediate composition but R_G takes the maximum value at the end point of x . Under the intimate relation of R_G to the ionic conduction as described in Sec. III, the different composition dependence of σ from that of R_G is not reasonable. However, if we employ the lowest energy of ω_{TO} , the maximum value of R_G/ω_{TO} appears at an intermediate composition, similar to that of σ . From this fact, the role of ω_{TO} seems to be fundamental.

The role of low frequency is further ascertained by comparing the R_G value with R_G/ω_{TO} value. The R_G/ω_{TO} values in several SIC's and HIC's are shown in Fig. 2. For the high frequency of ω_{TO} , the value of SIC MI ($M = \text{Ag, Cu}$) is not so different from that of HIC AgX ($X = \text{Cl, Br}$) despite the considerable difference of their σ values.² However, if we employ the lowest value of the ω_{TO} of Wurtzite (WZ)

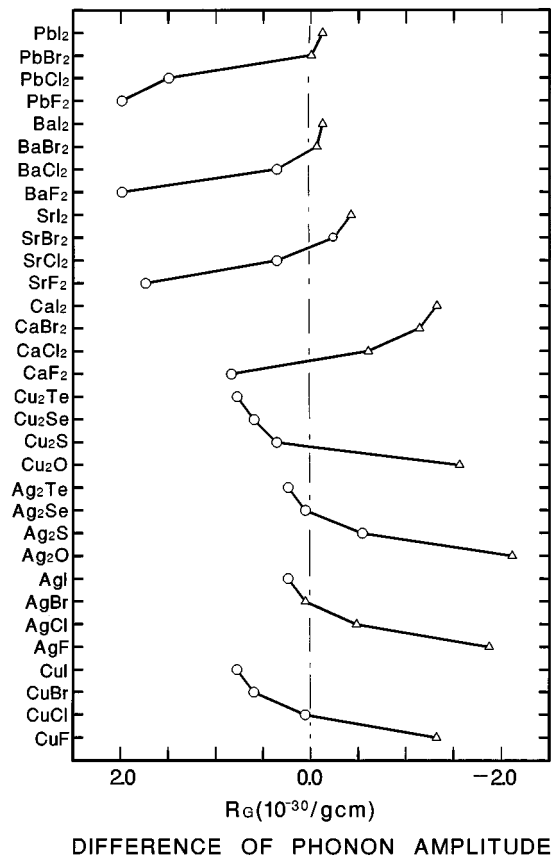


FIG. 1. The difference of vibration amplitude between mobile and cage ions in many SIC and related compounds. Circles and triangles indicate SIC's and non-SIC's, respectively. The chain is a basal line for classifying SIC's and non-SIC's.

type, the R_G/ω_{TO} in MI ($M = \text{Ag}$ or Cu) gives a considerably larger value than that in AgX ($X = \text{Cl}, \text{Br}$) or CuF . For example, the value for the E_2 mode at 17 cm^{-1} in $\beta \text{ AgI}$ (Refs. 40 and 41) is about five times larger than that for the E_2 mode at 106 cm^{-1} . This difference is correspondent to

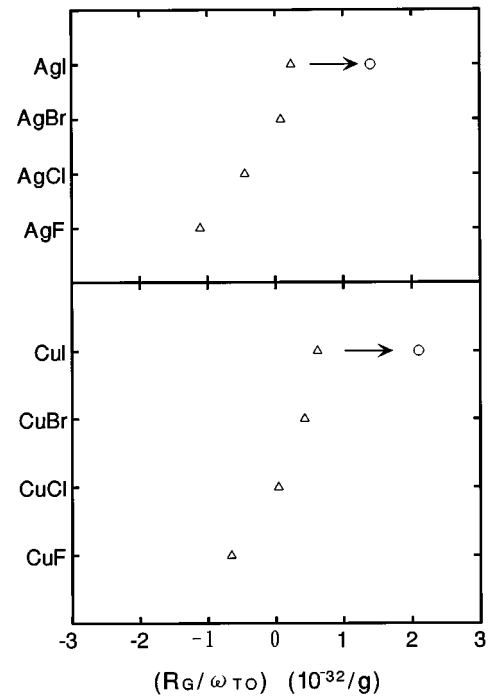


FIG. 2. (R_G/ω_{TO}) value in silver and copper halides. In AgF , AgI , and CuI , the values for 106 , 200 , and 128 cm^{-1} are shown by the triangles. For the latter two compounds, the values for 17 and 38 cm^{-1} , that are characteristic in WZ-type structure, are shown by the circles.

that of their σ values and, from this, we know the role of ω_{TO} to enhance the amplitude. For CuI and CuF , the feature is also similar.

B. Phonon assisted ionic conduction

To understand the role of the R_G/ω_{TO} value for the classification of SIC's and HIC's, we consider a model which combines the LEO phonon and mobile ion. A catapult, that easily shoots the mobile ions, is an example and it helps the

TABLE II. R_G values for $b = 1.0$ in cubic and near cubic ternary ionic conductors. An asterisk indicates the phonon mode relating to mobile ion vibration, predicted from the observed band width. Other symbols are the same as those in Table I.

Com. (ω_{ph}) (cm^{-1})	T_c (K)	R_G ($1/\text{g cm}$)	Ref. for phonon freq.
Ag_3SbI_5 -	-	-0.54×10^{30}	
$\text{Ag}_3\text{SbBr}(76)(28)^*$	118	-0.06	Wakamura and Hirokawa (Ref. 53)
$\text{Ag}_3\text{SI}(70)^*$	159	0.06	Wakamura <i>et al.</i> (Ref. 18)
$\text{PbCsCl}_3(80)$	310	0.72	Owens <i>et al.</i> (Ref. 60)
KCu_4I_5	530	0.60	
$\text{KAg}_4\text{I}_5(23)$	139	0.06	Burns <i>et al.</i> (Ref. 49)
KAg_4Br_4	-	-0.12	
$\text{RbAg}_4\text{I}_5(22)^*$	118	0.12	Delaney and Ushioda (Ref. 51)
$\text{Ag}_2\text{CdI}_4(14)^*$	353	0.12	Sudharsanan <i>et al.</i> (Ref. 61)
$\text{Cu}_2\text{CdI}_4(15)^*$	586	0.66	Sudharsanan <i>et al.</i> (Ref. 61)
$\text{Ag}_2\text{HgI}_4(24)^*$	324	0.18	McOmber <i>et al.</i> (Ref. 47)
$\text{Cu}_2\text{HgI}_4(37)^*$	340	0.72	McOmber <i>et al.</i> (Ref. 47)
$\text{Tl}_2\text{ZnI}_4(22)$	523	-0.21	Nitzan <i>et al.</i> (Ref. 17)

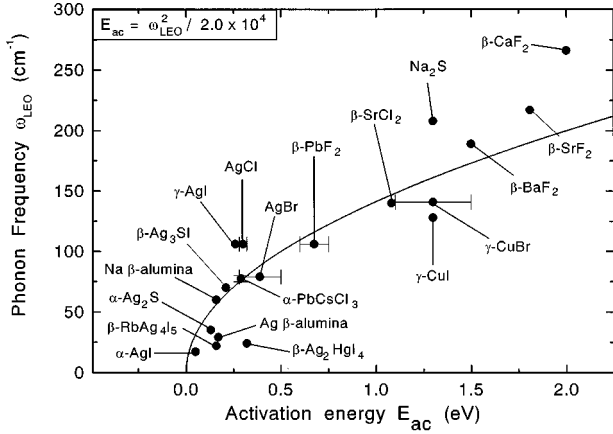


FIG. 3. Activation energy E_{ac} versus the lowest energy of optical phonon ω_{LEO} . A solid line is drawn with a relation as $E_{ac} = \omega_{LEO}^2/20\,000$. The data for E_{ac} and ω_{LEO} are taken from Refs. 1, 2, 58, 59, and from Refs. 3 and 5, respectively.

jump of mobile ions with a large phonon amplitude. In particular, the LEO phonon incorporating the mobile ion contributes dominantly to such a jumping, as mentioned in Sec. IV A. This result is evident from the coexistence of the LEO phonon and the low- T_c value in the mobile ion type SIC in Tables I and II. This feature seems to be particularly noticeable in ternary compounds since those possess the LEO phonon at low temperature. Such a phonon can shoot the mobile ions even at low temperature.

The second evidence is the correlation between the E_{ac} value and the energy of the LEO phonon ω_{LEO} . Both the values are plotted in Fig. 3. Clear regularity appears and it presents the activation energy depending on the phonon amplitude. For the expression of regularity, a simple form is employed. Since the nature of the LEO phonon is acousticlike,^{23,25,41} the correlation for the acoustic phonon in the self-diffusion of bcc metal,²⁴ in which the crystal energy is expressed in terms of square of the frequency of the longitudinal acoustic phonon at the $2\langle 111 \rangle/3$ point of the Brillouin zone,²⁴ is referred to as

$$E_{ac} = C\omega_{LEO}^2. \quad (7)$$

To obtain a good regularity for the plotted points, we employ $1/20\,000$ for the C value. The curve is drawn by the solid line in Fig. 3. The agreement is excellent and it may reveal that the LEO phonon contributes dominantly to the mobile ions with a manner similar to that of the acoustic phonon in bcc metals.²⁴ This similarity of the manner is further supported from a linear relationship between the melting temperature T_m and the phonon frequency ω_{ph} established in bcc metal and SIC's, in which the ω_{ph} in bcc metal is the acoustic phonon at the $\langle 111 \rangle$ direction of the Brillouin zone and the ω_{ph} in the SIC is the ω_{LO} value.⁴ Further, from the dominant effect of the d -electron charge density on the ionic conduction, that appears in both bcc metals²⁴ and SIC's,³⁻⁶ we can support the similarity.

The importance of the vibration phase, though it presents the cooperative relation for the mobile ion and the optical phonon as treated in molecular dynamics⁴² is pointed out by Wakamura.²⁵ Because the zone center phonon contributes

more dominantly to the ionic motion in SIC's, he suggests qualitatively the directions of vibrational ions, in which an optical mode vibrates the mobile ions in the nearest-neighbor unit cell for the same direction but the zone boundary acoustic phonon vibrates the ions for the opposite direction.²⁵ The energy and the vibrational phase of the LEO phonon are characterized by the zone boundary acoustic phonon and the zone center optical phonon, respectively.

To shoot defects effectively, the LEO phonon must incorporate the mobile ions. We can show this for SIC's. In the binary compounds, the incorporation of the mobile and cage ions is obvious since the dipole moment for the vibration is composed of both the anion and cation. A typical example is seen in the remarkable broadening of the E_2 mode at 17 cm^{-1} near T_c in AgI.^{40,41} In CuI, the fundamental phonon mode is at 128 cm^{-1} , however, another band appears at 38 cm^{-1} , which arises from WZ-type symmetry due to the deformation of the Cu ion,⁴³ and, therefore, a large phonon amplitude similar to that of the 17 cm^{-1} mode in AgI is also anticipated. In CuCl, a LEO phonon has not been clearly reported, however, the existence of it may be expected because of the similar crystal structure, in which the Cu ions occupy the off center positions as suggested by Hochheimer *et al.*,¹⁶ Vardeny and Brafman,⁴⁴ Boyce, Hayes, and Mikkelsen, Jr.,⁴⁴ and Kanellis, Kress, and Bilz.⁴⁵ In β CuBr, we anticipate the LEO phonon from the crystal structures of the γ and β phases, which take, respectively, zinc blende (ZB)- and WZ-type structures similar to AgI. Further, Turner *et al.*⁴⁶ observed a rapid decrease of the TO phonon frequency with increasing temperature below room temperature, and predicted a near zero value at T_c by extrapolation. This phonon mode can play the same role as that of the LEO phonon because it is a zone center phonon having low energy.

For the ternary SIC, the incorporation is also ascertained by noting the broadening of the peaks that appears for the vibrational mode involving movable Ag ions, as indicated clearly in AgCrS_2 .^{29,30} In $M_2\text{HgI}_4$ ($M = \text{Ag, Cu}$), when the E mode is at 25 cm^{-1} there is an extremely large broadening of the Raman band at and above T_c .^{47,48} This is evidence for the incorporation. Leduc and Coleman suggest a tight coupling of the mode with mobile ions.⁴⁸ In the Raman spectra of RbAg_4I_5 , the broadening of the peaks near 20 and 30 cm^{-1} appears suddenly at T_c .⁴⁹⁻⁵¹ This is also evidence for the incorporation.

In β - and γ - Ag_3SX ($X = \text{I, Br}$), three infrared active modes are predicted from the symmetry of antiperovskite-type crystal.⁵² However, only two modes have been observed.^{18,53} According to the calculation of lattice dynamics,⁵² another mode incorporating the Ag ion of bending type should be observed at lower energy. This phonon may correspond to the band at low energy observed by Hoshino *et al.*⁵⁴

C. Predicted behaviors

Using Eq. (6) and the R_G/ω_{TO} value, we can understand some of the phenomena characteristic in SIC's, which support the proposal in this paper. First, the pressure dependence of ionic conductivity in general shows bowing with pressure.^{55,56} The cause of it can be understood within first approximation using the R_G value. If we assume a linear

proportionality for the ionic radius of the mobile ion, decreasing with pressure as $r_X = r_{X0} - \alpha p$ and $r_A = r_{A0} - \beta p$, then the R_G value in Eq. (6) can be expressed as $R_G = [(m_X r_{X0} - r_{A0} m_A) - p(\alpha m_X - \beta m_A) / m_A m_X b \{r_{X0} r_{A0} - p(\alpha r_{A0} + \beta r_{X0})\}]$. For positive values of $(\alpha m_A - \beta m_X)$, the R_G value shows bowing in the upper direction with pressure, so it must increase the probability of the mobile ion jump. That is in accordance with the bowing for the pressure dependence of σ as observed in Refs. 55 and 56.

The second characteristic is the absence of superionic conduction of Au chalcogenides. For these chalcogenides, Eq. (6) takes a negative value because the atomic mass of the mobile Au ion is heavier than that of the chalcogen ion, as listed in Table I. Therefore, the absence of superionic conduction is likely. This prediction is consistent with the small ionic transfer number of gold measured in Au₂S.⁵⁷

V. CONCLUSION

The elemental factor realizing superionic conduction was semiquantitatively established using an equation of motion in

terms of atomic mass, ionic radius, and phonon frequency. This was based on a hypothesis that the force field around mobile and cage ions was different. The criterion, which distinguishes the SIC, is the vibrational amplitude of mobile ions being larger than that of the cage ion, and the noninteger value of chemical valence. The classification of SIC's based on the vibrational amplitude was achieved for many binary and ternary compounds. Together with the relationship between E_{ac} and ω_{ph} , we ascertained empirically the lowering of activation energy, assisted by enhanced phonon amplitudes. Based on these results, we understood qualitatively some of the characteristic phenomena of SIC's.

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