

## Origin of the low-energy mode in superionic conductors

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The energy of phonon modes in the  $\beta$  phase of AgI is estimated from the phonon modes of the  $\gamma$  phase since the Brillouin zone ( $B$  zone) of the former phase can be obtained by folding that of the latter. The idea of folding the Brillouin zone is extended to other binary and ternary superionic conductors (SIC's). Then the low-energy mode, which is observed for many SIC's at the center of the  $B$  zone, is assigned to an optical phonon at the lowest frequency (LEO phonon), originating from a transverse-zone-edge acoustic phonon. The proportionality of mode frequency with the inverse square root of mobile ion mass, the pressure and temperature dependencies of the mode frequency, and the close relationship of the LEO phonon to the low transition temperature are understood from the result of folding the  $B$  zone with respect to the specific crystal structure of the SIC's. [S0163-1829(99)06305-5]

### I. INTRODUCTION

The effect of the  $d$  electron on high ionic conduction of superionic conductors (SIC's) is pointed out from the specific dielectric properties,<sup>1-4</sup> and also from the Jahn-Teller effect,<sup>5</sup> the chemical bonding,<sup>6</sup> and the electron-hole pair,<sup>7</sup> which are related to  $p$ - $d$  hybridization near the top of the valence band.<sup>8-12</sup>

However, we can not classify clearly SIC's and non-SIC's from only such dielectric properties described above. AgF is an example since it exhibits a specific dielectric property due to the substantial hybridization of  $\text{Ag}^+ 4d$ ,  $\text{F}^- 2p$ , and  $\text{F}^- 2s$  levels<sup>13</sup> but not as a SIC.

Concerning these facts, Wakamura has described the role of the phonon amplitude in superionic (SI) conduction,<sup>14</sup> and suggests that the lowest frequency phonon (LEO phonon) enhances the vibrational amplitude and assists the increase of defects. In order to study the mechanism for producing defects microscopically, the origin of the LEO phonon should be deduced.

On the other hand, the existence of a band at low energy or low-energy (LE) mode is characteristic of SIC's and has been observed using optical<sup>15-19</sup> and neutron<sup>20</sup> spectra. However, this band has not been assigned uniquely, though such causes as a phonon mode,<sup>21-23</sup> an attempt mode of diffusive ions,<sup>24</sup> an ion plasma mode,<sup>25</sup> and a local mode<sup>26</sup> have been considered.

In this paper, we elucidate the origin of the LEO-phonon mode and its relation to the LE mode by considering the relationship between the crystal structure and the phonon dispersion. In Sec. II, the experiments are explained. In Sec. III, the phonon spectra for the  $\beta$  and  $\gamma$  phases of AgI are shown as a function of temperature. Based on these results, we propose the folding of the Brillouin ( $B$ ) zone in Sec. IV to explain the phonon-dispersion curve using a similar consideration when interpreting the crystal poly-type structure.<sup>27</sup> In Sec. V, the folding of the  $B$  zone is used to explain the optical phonon bands distributed at two separated energy regions. In Sec. VI, the relationship is extended to Cu halides, ternary SIC's, group II-VI chalcogenides, and Ag and Cu chalcopyrite compounds. Characteristic phenomena of the LE mode in these SIC's, for example, negative pressure and small temperature dependencies of the frequency and the fre-

quency proportional to the inverse mobile ion mass, are interpreted from the properties of the LEO phonon. In Sec. VII, the appearance of the LEO phonon is related to the low  $T_c$  value and the specific crystal structure of SIC's. Further, nonsuperionic conduction in the cubic AgX ( $X = \text{F}, \text{Cl}, \text{Br}$ ) is understood by noticing the nonexistence of the LEO phonon in AgX. From these interpretations, the LE mode is identified as the LEO-phonon mode.

### II. EXPERIMENTS

A pressed pellet of  $\gamma$  [zinc-blende(ZB) structure]-AgI, with an 11-mm radius and 3-mm thickness, was obtained from powdered crystals under a pressure of 5000 kg/cm<sup>2</sup> at room temperature for 2 h. A pressed pellet of  $\beta$  [wurtzite (WZ) structure] phase was obtained under 2000 kg/cm<sup>2</sup> at room temperature, and then kept at 142°C for 7 days.<sup>28</sup> X-ray diffraction spectra for each phase of the crystal gave only diffraction peaks characteristic of the structure of the  $\beta$  or  $\gamma$  phase.

To omit reflected light from the back surface, the sample was cut into a wedge shape and the front surface ground until it was optically flat. The temperature of the copper sample holder was measured by a constantan Fe (0.07% Au) thermocouple and calibrated using the transition temperature of Ag<sub>3</sub>SI.<sup>29</sup> Reflectivity measurements were made from 700 to 15 cm<sup>-1</sup> with a resolution of 1 cm<sup>-1</sup> at various temperatures using a Fourier-transform spectrometer (Degilab Inc. 20E/D). The reference signal of reflected light was obtained using an optically flat Au mirror.

### III. EXPERIMENTAL RESULTS

Measured reflectivity spectra for the  $\gamma$  and  $\beta$  phases in AgI are shown in Fig. 1 as a function of temperature. Near room temperature, the phonon spectra in both the phases exhibit almost the same structure. Of the observed bands, the  $a$  and  $b$  bands have already been assigned as the fundamental and two-phonon bands, respectively.<sup>13,19,20,30,31</sup> The  $a$  band splits at low temperature. The dielectric constant  $\epsilon(\omega)$  is calculated as a function of frequency from the measured reflectivity.

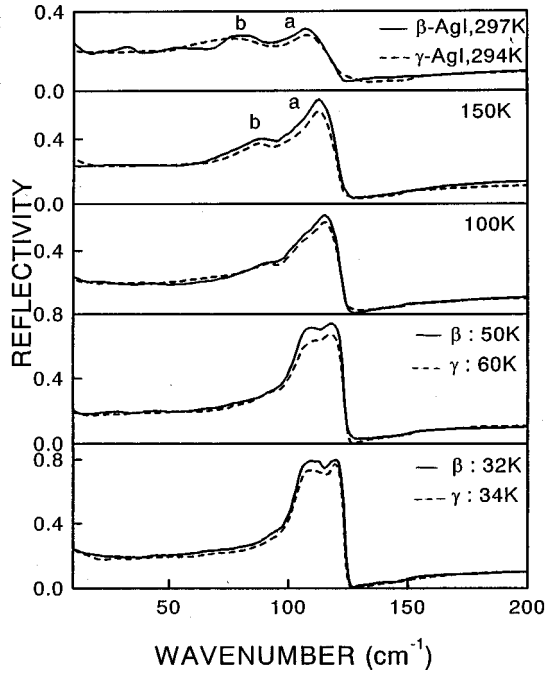


FIG. 1. Reflectivity spectra in the  $\gamma$  and  $\beta$  phases of pressed pellets of AgI at various temperatures.

tivity spectra with the Kramers-Kronig relation. The frequencies of transverse-optical (TO) and longitudinal-optical (LO) phonon modes are determined from the frequency positions of the peaks of  $\text{Im}(\epsilon)$  and  $\text{Im}(1/\epsilon)$ , respectively.<sup>32</sup> The values are listed in Table I. The optical dielectric constant  $\epsilon_\infty$  is determined from the  $\epsilon(\omega)$  value at  $700 \text{ cm}^{-1}$ .

#### IV. BRILLOUIN ZONE AND CRYSTAL STRUCTURE IN AgI

Based on the observed results, we deduce the origin of the LEO phonon with respect to the phonon dispersion relation of WZ type. The  $A$  and  $E$  modes in WZ-type AgI exhibit the same frequency within experimental error, as listed in Table II.<sup>19,20,30,31</sup> In Fig. 2, the TO-LO splitting and the frequency shift with temperature for the  $\beta$  and  $\gamma$  phases are shown to be almost equal. These results suggest that the dielectric property and atomic arrangements at the local regions are almost the same in the  $\beta$  and  $\gamma$  phases. Further, the x-ray diffraction pattern of the  $\beta$  phase, characteristic of WZ-type structure, implies a primitive unit cell of WZ type that contains two cells with the symmetry similar to that of ZB type. From this fact, we can combine the  $B$  zone in the ZB structure with that of the WZ structure, as described in the next section.

TABLE I. Determined phonon frequencies ( $\text{cm}^{-1}$ ) and  $\epsilon_\infty$  values in  $\beta$  and  $\gamma$  phases of AgI.

Phase	$\epsilon_\infty$		$\omega_{\text{TO}}$		$\omega_{\text{LO}}$	
	32 K	296 K	32 K	296 K	32 K	296 K
$\beta$	4.6	4.9	104.3	105.6	124.0	120.9
$\gamma$	4.6	4.7	104.0	105.8	123.0	119.8

TABLE II. Phonon frequencies of AgI and CdS estimated by folding the  $B$  zone. The symbols, ZF (zone folding), WZ (calc.), WZ (obs.) in the first column indicate the values estimated from folding the  $B$  zone of ZB structure, and calculated (Refs. 20 and 58) and observed (Refs. 30 and 58) values, respectively. The symmetry of the mode given in the brackets is slightly different for the theoretical and experimental analyses.

	ZF ( $\text{cm}^{-1}$ )	WZ (calc.) ( $\text{cm}^{-1}$ )	WZ (obs.) ( $\text{cm}^{-1}$ )
CdS	41.1	42.8	42
	177.4	167.3	170
	220.2	206.6	200–210
	243.5	235.9	243
	256.7	252.8	256
	310.3	293.8	305
AgI	17.6	17.8( $E_2$ )	17( $E_2$ )
	65.9	68.1	
	108.3	108.1( $E_1$ )	106( $A_1, E_1$ )
	112.0	111.1( $A_1$ )	112( $E_2$ )
	113.7	113.5( $E_1$ )	
	120.9	123.0( $A_1$ )	124( $A_1, E_2$ )

#### V. ZONE FOLDING AND LOW-ENERGY OPTICAL PHONON

We propose the folding of  $B$  zone for the  $\beta$  (WZ-type) and  $\gamma$  (ZB-type) phases of AgI. The unit cell of WZ type has approximately twice the volume of the unit cell of ZB type. The ZB type takes the unit cell with rhombohedral form having the edge length of  $4.57 \text{ \AA}$ , though the lattice constant for the cubic form is  $6.47 \text{ \AA}$ .<sup>33</sup> Since the lattice constant for the  $a$  axis of WZ type is  $4.58 \text{ \AA}$  that is nearly equal to  $4.57 \text{ \AA}$ , the volume of WZ type is characterized by the lattice constant for the  $c$  axis,  $c_w = 7.5 \text{ \AA}$ , which is roughly twice the value of  $4.57 \text{ \AA}$ . Then the wave vectors at the edge of the  $B$  zone for the ZB and WZ types can be represented approxi-

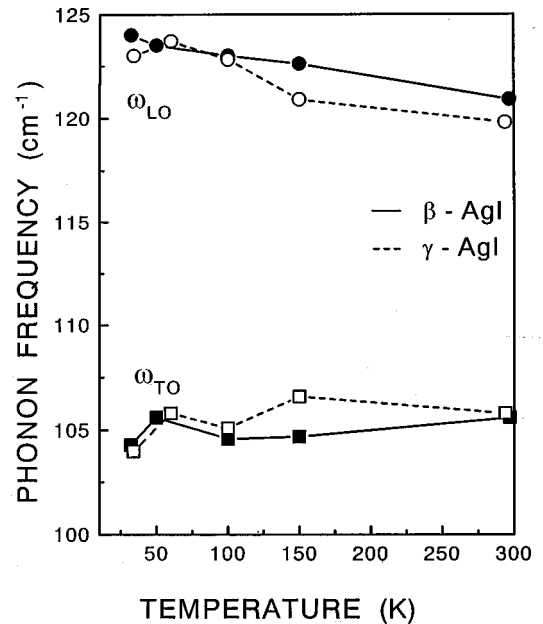


FIG. 2. Temperature dependence of phonon frequencies in AgI.

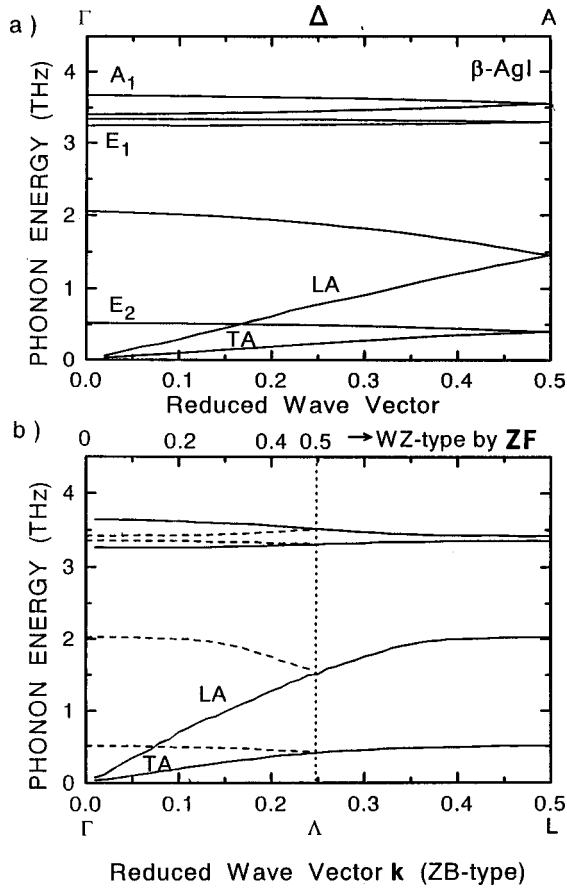


FIG. 3. Phonon dispersion curves of ZB and WZ types of AgI. (a) Calculated from the lattice dynamics of WZ type (Ref. 34). (b) The  $B$  zone of ZB-type structure (Ref. 20) and the curve from folding the  $B$  zone are shown by solid and dashed lines, respectively.

mately by the  $c_w$  values,  $k_z = \pi/(c_w/2)$  and  $k_w = \pi/c_w$ , respectively. The equality  $k_z = 2k_w$  is realized and it reveals that the zone edge in the ZB type is equivalent to the zone center in the WZ type. Hence the phonon dispersion of the WZ type for the  $c$  axis will be obtained approximately by folding the dispersion curve at the midpoint between the zone edge and the center of the  $B$  zone in ZB-type  $\gamma$ -AgI.<sup>20</sup> This equality is understood conceptually by employing linear chains composed of one and two constituent atoms under one and two times the periodicity of the crystal lattice, respectively.

We estimate the phonon-dispersion curve from the  $\Gamma$  to A points of the  $B$  zone in the  $\beta$  phase of AgI from that of  $\gamma$  phase by folding the  $B$  zone at the midpoint between the zone center and the zone edge. Those values are shown by a dashed line in Fig. 3(b). The zone-center phonons originating from the optical ( $E, A$  modes) and longitudinal-acoustic (LA) and transverse-acoustic (TA) phonons at the zone edge appear separately at high- and low-energy positions, respectively. The energy of these modes is in good agreement with the phonon energy calculated from the lattice dynamics,<sup>20,34</sup> shown by a solid line in Fig. 3(a), and also with that of the LE mode. This excellent result supports the assumption described above.

The frequency of the LEO phonon  $\omega_{LEO}$ , estimated from the dispersion of phonon modes in Figs. 3(a) and 3(b), is

listed under the headings WZ (calc.) and ZF in Table II, respectively. The values are in agreement with the observed frequency in the column of WZ (obs.) within 10% and also with the frequency of the LE mode  $\omega_{LE}$  in Table III. We obtained similar results for CuX ( $X = \text{Cl}, \text{Br}, \text{I}$ ).

Because of these excellent results, we can conclude that the LEO phonon originated from the zone-edge acoustic phonon (ZEA phonon). When the  $B$  zone can be folded, a LEO phonon is present. Therefore we propose a rule that the crystal lattice constructed from plural units under similar atomic arrangements must be connected to the existence of the LEO phonon. Such units in SIC's may be caused by the enhanced effective charge due to the  $p$ - $d$  hybridization, as discussed already.<sup>3</sup>

According to this rule, the LEO phonon cannot exist in cubic CuF and AgX ( $X = \text{F}, \text{Cl}, \text{Br}$ ), since these compounds do not have a unit cell composed of plural units with similar atomic arrangements. To confirm this rule, we apply it to binary and ternary SIC's, as discussed in the next section.

## VI. APPLICATION OF THE $B$ -ZONE FOLDING TO SIC'S

By applying the procedure of folding the dispersion curve, we can show excellent results for many SIC's. In this section, a general relationship between the LEO phonon and the specific crystal structure will be offered for typical group II-VI and chalcopyrite compounds.

### A. Application to Cu and Ag halides

In the  $\beta$  and  $\gamma$  phases of CuX ( $X = \text{Cl}, \text{Br}, \text{I}$ ),<sup>35</sup> the crystal structure is equivalent to that of AgI. Since the unit cell in the  $\beta$  phase is composed of two units with similar atomic arrangements,<sup>20</sup> the rule for folding of the  $B$  zone is satisfied and we can predict an edge like the LEO phonon in the same manner as described in Sec. V. Such a property is clearly observed in CuBr (Refs. 36 and 37) and CuI.<sup>37,38</sup> Estimated frequencies, listed in Table III, are in agreement with the values calculated from the lattice dynamics of the WZ type.

In CuCl, we can also anticipate the existence of the LEO phonon because the crystal structure is similar to that of CuX ( $X = \text{Br}, \text{I}$ ). Although the existence of the mode is unclear from experiments,<sup>39</sup> it has been suggested theoretically by Aniya, Tomoyose, and Kobayashi.<sup>40</sup>

### B. Application to ternary compounds

We can apply the folding of the  $B$  zone to the lowest temperature crystal phase in a ternary SIC because the phase is composed of plural units having slightly different atomic sites and satisfies the rule proposed in Sec. V. Then, the LEO phonon appears in this phase, as listed in Table IV. Several examples are offered below.

In the crystal structure of  $\text{Ag}_3\text{SX}$  ( $X = \text{Br}, \text{I}$ ), the antiperovskite-type structure appears in the  $\beta$  and  $\gamma$  phases, as listed in Table IV, in which Ag ion occupies one of four disorderly off-center positions on the surface of the perovskite-type unit.<sup>29</sup> The existence of such units may induce dipole moments and ferroelectric transitions.<sup>41</sup> If the long-range periodicity is realized by these units, the  $B$  zone can be folded as before (Sec. V). Performing this, several zone-center phonons originating from the ZEA and optical phonons appear at two separated frequency regions.

TABLE III. The frequency ( $\text{cm}^{-1}$ ) of the LEO phonon at  $k=0$  estimated from folding the  $B$  zone and that calculated from the dispersion curve of WZ structure, the observed frequency of phonon mode, and observed and calculated frequencies of the LE mode, which are listed in the columns ZF, WZ (calc.), WZ (obs.),  $\omega_{\text{LE}}$  (obs.), and  $\omega_{\text{LE}}$  (calc.), respectively. The values in the parentheses are indicated in units of meV. The references for the observed values are listed under the heading Ref.

Compound	ZF	WZ (calc.)	WZ (obs.)	$\omega_{\text{LE}}$ (obs.)	$\omega_{\text{LE}}$ (calc.)	Ref.
Cation SIC's						
$\beta$ -AgI	17(2.2)	18(2.3)	17(2.2)	17(2.2)	(2.6) <sup>a</sup> (3.5) <sup>a</sup> (8.6, 9.3–12) <sup>b</sup>	19, 20
CuCl	38(4.7)	34(4.2)				36, 37
CuBr	38(4.7)	28(3.5)				36, 81
CuI	34(4.2)	32–35 (3.9–4.3)		27(3.4)		36, 38
$\alpha$ -Ag <sub>2</sub> S				16(2.0)	(3.5 <sup>b</sup> , 4.1 <sup>a</sup> )	73
$\beta$ -Cu <sub>2</sub> Se				27(3.4)	40(5.0) <sup>a</sup>	16
Ag-Al <sub>2</sub> O <sub>3</sub>	45(5.6)			22(2.7)	(1.3) <sup>a</sup>	50–53
Na-Al <sub>2</sub> O <sub>3</sub>	45(5.6)			40–48(5–6)	22(2.7) <sup>a</sup>	50–53
Anion SIC's (cubic fluorite type)						
CaF <sub>2</sub>	146(18.1)			257 <sup>c</sup>		74, 82
BaF <sub>2</sub>	67(8.3)			184 <sup>c</sup>		74, 82
SrF <sub>2</sub>	93(11.5)			217 <sup>c</sup>		74, 82
PbF <sub>2</sub>	58(7.2)			102 <sup>c</sup>		83
SrCl <sub>2</sub>	64(7.9)			79 <sup>c</sup>		84, 85
UO <sub>2</sub>	93(11.5)			280 <sup>c</sup>		86
Nonionic conductor						
ZnO	101(12.5)	100(12.4)	101( $E_2$ )			87
ZnS	69(8.4)	50(6.2)				87
ZnSe	48(6.0)	41(5.1)				87
ZnTe	38(4.7)	33(4.1)				87
CdSe	45(5.6)	34(4.2)				87
CdTe	35(4.3)	31(3.8)				87

<sup>a</sup>The ionic plasma model (Refs. 25 and 68).

<sup>b</sup>Hubbard-Beeby model (Refs. 76 and 79).

<sup>c</sup>TO phonon at  $k=0$ .

Shibata and Hoshino observed a LE mode by neutron-scattering measurements,<sup>42</sup> and Wakamura and co-workers observed several peaks in far-infrared spectra in the  $\gamma$  phase of Ag<sub>3</sub>SX ( $X = \text{Br}, \text{I}$ ).<sup>43,44</sup> The number of observed peaks is greater than that predicted from the crystal symmetry of perovskite structure. This fact supports the existence of the plural units mentioned above.

$M\text{Ag}_4\text{I}_5$  ( $M = \text{Rb}, \text{K}$ ) exhibits three crystal phases listed in Table IV. The  $\gamma$  phase contains four formula units with slightly different atomic arrangements.<sup>45,46</sup> This structure gives several units with slightly different positions of the Ag ion, and so the crystal lattice will have a long-range periodicity. By again folding the  $B$  zone depending on the length of periodicity, we can predict many zone-center phonons originating not only from the zone-edge phonons but also from the phonons at the intermediate points between the center and the edge of the  $B$  zone. These bands occupy two separated energy regions as suggested in Sec. V, and agree with previous results.<sup>26,47–49</sup>

In  $M$  ( $M = \text{Ag}, \text{Na}$ )  $\beta$ -alumina, we anticipate a long-range periodicity since the unit cell is composed of four blocks with spinel structure along the  $c$  axis, involving two  $M$  ions. The lattice constant for the  $c$  axis is approximately four times the length of that for the  $a$  axis, but  $\epsilon_\infty$  values for both

directions are nearly equal.<sup>50–52</sup> From these facts, we predict near isotropy of the local region and slight deviation of the atomic sites from the cubic symmetry. Since this structure satisfies the rule described in Sec. V, the frequency of the LEO phonon is estimated from folding the dispersion curve of the acoustic phonon at the zone edge.<sup>53,54</sup> The obtained value is in good agreement with the observed value, as listed in Table III.

Several more bands appear below  $50 \text{ cm}^{-1}$ , though the number of bands depends on the crystal growth.<sup>53–56</sup> These bands can be understood from the folding of the  $B$  zone two times.<sup>54</sup> Two bands at low energy are obtained near 6 and 3 meV. The energy of the latter band is near the observed frequency of the LE mode, 2.8 meV. Other bands in different crystal axes<sup>50–54</sup> can also be assigned by folding the  $B$  zone.

In a defect-type chalcopyrite,  $M_2NX_4$ , two phases exist, as shown in Table IV. The crystal structure of the  $\beta$  phase has four units with ZB structure under slightly deformed atomic arrangements.<sup>55–57</sup> Since this structure allows the possibility for long-range periodicity, we can predict many phonon bands by folding the  $B$  zone. The LEO phonon and the many bands are clearly observed at two separated frequency regions.<sup>55–57</sup>

TABLE IV. Crystal structure and transition and melting temperatures in binary and ternary ionic conductors and related compounds. The frequency of the LEO phonon is listed in parentheses. The symbols  $\alpha$ ,  $\beta$ , and  $\gamma$  indicate the phase of crystals. The data are employed from the references in the Ref. column of Table III together with the Refs. 1, 12, 71, 72, 75, and 88–90. RC: rocksalt type. WZ: wurtzite type. ZB: zinc-blende type. CF: cubic fluorite. Sb: sublimation.

Compound	TO phonon ( $\text{cm}^{-1}$ )	$T_{c1}$ (K)	$T_{c2}$ (K)			$T_m$ (K)
			High ionic conductor			
AgF	(170)	RC				708
AgCl	(106)	RC				722
AgBr	(79)	RC				692
CuF	( )	RC				
Cu <sub>2</sub> O	(100)	Cubic				1230
Mobile ion-type SIC					SIC <sup>b</sup>	
CuCl	(172)	$\gamma$ (ZB)	680	$\beta$ (WZ)		695–708
CuBr	(141)	$\gamma$ (ZB)	664	$\beta$ (WZ)	743	$\alpha$ 761
CuI	(128)	$\gamma$ (ZB)	642	$\beta$ (WZ)	680	$\alpha$ 874
AgI	(17)	$\gamma$ (ZB)	410	$\beta$ (WZ)	419	$\alpha$ (bcc) 803
Ag <sub>2</sub> S	(36)	mono	450	$\beta$ (bcc)	866	$\alpha$ (fcc) 1098
Ag <sub>2</sub> Se	( )	mono	406	$\beta$	430	$\alpha$ (fcc) 1153–1170
Ag <sub>2</sub> Te	( )	mono			415	$\alpha$ (fcc) 1228
Cu <sub>2</sub> S	( )	$\gamma$	376	$\beta$ (hexa)	717	$\alpha$ (cubic) 1373
Cu <sub>2</sub> Se	( )	$\gamma$	203	$\beta$	383	$\alpha$ 1386
Cu <sub>2</sub> Te	( )	$\gamma$	624	$\beta$	660	$\alpha$
Ternary compound SIC					SIC <sup>b</sup>	
Ag <sub>3</sub> SI	(75)	$\gamma$	157	$\beta$	519	$\alpha$
Ag <sub>3</sub> SBr	(85)	$\gamma$	118	$\beta$	dissociation	
CsPbCl <sub>3</sub>	(28)	$\gamma$	310	315	320(cubic)	604–610
KAg <sub>4</sub> I <sub>5</sub>	(17)	$\gamma$	139	$\beta$	194	$\alpha$ (cubic) 526
KCu <sub>4</sub> I <sub>5</sub>	( )	$\gamma$		$\beta$	530	$\alpha$
RbAg <sub>4</sub> I <sub>5</sub>	(17)	$\gamma$ ( $D_3^2$ )	122	$\beta$	209	$\alpha$ 501
NH <sub>4</sub> Ag <sub>4</sub> I <sub>5</sub>	(18)	$\gamma$	135	$\beta$	199	$\alpha$ 505
Defect-type SIC						SIC <sup>b</sup>
CaF <sub>2</sub>	(257)			$\beta$ (CF)	1430	$\alpha$ 1673
CaCl <sub>2</sub> <sup>a</sup>	( )			Orthorhombic		1055
SrF <sub>2</sub>	(217)			$\beta$ (CF)	1400	$\alpha$ 1733
SrCl <sub>2</sub>	(147)			$\beta$ (CF)	990	$\alpha$ 1146
SrBr <sub>2</sub>	( )			$\beta$	918	$\alpha$ 1043(Sb)
BaF <sub>2</sub>	(184)			$\beta$ (CF)	1235	$\alpha$ 1553
BaCl <sub>2</sub> <sup>a</sup>	( )			(CF)	1193	1231
PbF <sub>2</sub>	(106)			$\beta$ (CF)	705	$\alpha$ 1128–1158
PbCl <sub>2</sub>	( )			$\beta$	703	$\alpha$ 772
UO <sub>2</sub>	(280)			$\beta$ (CF)	2573	$\alpha$ 3138
ThO <sub>2</sub>	(279)			$\beta$ (CF)		$\alpha$ 3523
Na <sub>2</sub> S	(208)			$\beta$ (CF)	1273	$\alpha$ 1450
Ag <sub>2</sub> HgI <sub>4</sub>	(36)			$\beta$	323	$\alpha$
Cu <sub>2</sub> HgI <sub>4</sub>	(16)			$\beta$	344	$\alpha$ 1073
Ag <sub>2</sub> CdI <sub>4</sub>	( )			$\beta$	353	$\alpha$ 418
Cu <sub>2</sub> CdI <sub>4</sub>	( )			$\beta$	586	$\alpha$

<sup>a</sup>Nonsuperionic conductor.

<sup>b</sup>SI-conduction phase.

### C. Application of the *B*-zone folding in nonsuperionic conductors

The folding of the *B* zone is applied to non-SIC's, such as group II-VI chalcogenides,<sup>27,58</sup> and Cu and Ag chalcopyrite

compounds.<sup>59–62</sup> This result shows a general correlation between the LEO phonon and the long-range periodicity of crystal structure.

In group II-VI compounds, the WZ-type crystal has approximately twice the periodicity of the atomic arrangement

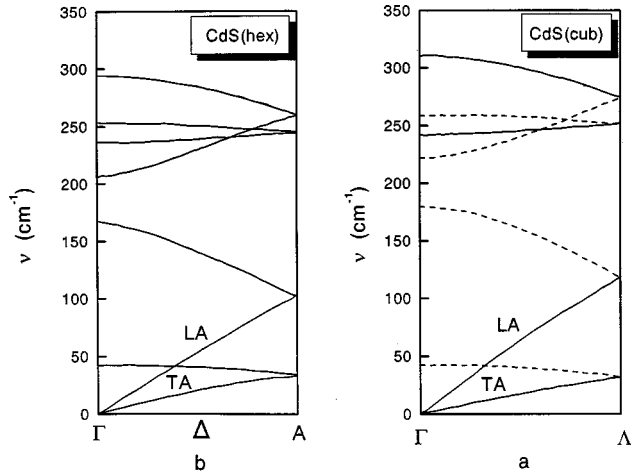


FIG. 4. Phonon-dispersion curves of CdS. (a) The dispersion curve of ZB-type structure (Ref. 58) and the curves estimated from folding the  $B$  zone are shown by solid and dotted lines, respectively. (b) The dispersion calculated from the lattice dynamics of WZ-type CdS (hexa) (Ref. 58).

in the ZB type. Therefore, the phonon dispersion in the WZ type is obtained by folding the  $B$  zone of the ZB type. An example is shown in Fig. 4. The dispersion curve of CdS is drawn by a dashed line and agrees closely with that calculated from the lattice dynamics for the WZ type [Fig. 4(b)].<sup>58</sup> The estimated frequency is listed in Table II. The  $\omega_{\text{LEO}}$  values for other group II-VI compounds with WZ structure are listed in Table III. In particular, the  $\omega_{\text{LEO}}$  values in ZnO (Refs. 63–65) and CdS (Ref. 58) are in good agreement with the observed values, and also with the values calculated from the lattice dynamics of the WZ type.<sup>58,63–65</sup>

In normal chalcopyrite compounds, the nature of phonon modes at the  $\Gamma$  point is predicted from the dispersion at  $\Gamma$  and  $X$  points in the  $B$  zone of ZB type.<sup>59–62</sup> A LEO phonon is observed in  $\text{AgCrSe}_2$  (Refs. 59 and 60) and other compounds.<sup>61,62</sup>

## VII. DISCUSSION

Based on the folding of the  $B$  zone, the characteristic behaviors of the LE mode are described in relation to the properties of the LEO phonon in a SIC, proving the equivalence of the LE mode and the LEO-phonon mode. Next, we discuss the appearance of the LEO phonon induced from the specific crystal structure in a SIC. A relationship between the LEO phonon and the presence of low transition temperature is also suggested.

### A. Specific properties of the LEO phonon

Specific properties of the LE mode are negative pressure dependence<sup>66,67</sup> and an extremely small temperature dependence. The same properties are also anticipated for the LEO phonon,<sup>40,68</sup> as observed on the  $E_2$  mode of  $\text{AgI}$ ,<sup>66</sup>  $\text{Ag}_2\text{HgI}_4$ ,<sup>67</sup> CdS, ZnO, and ZnS with WZ structure.<sup>69,70</sup> Since the property of the LEO phonon is characterized by a transverse ZEA phonon, the frequency is dominated by the shear force constant, as suggested by Bühren and Brüesch,<sup>34</sup> and it has negative pressure dependence, shown by the negative value of the Grüneisen-mode parameter.<sup>70</sup>

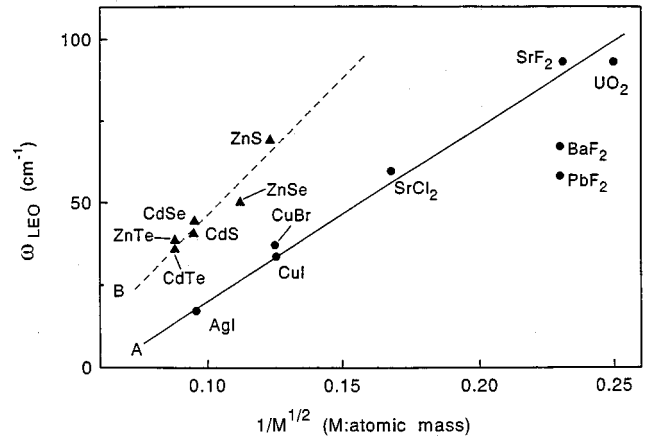


FIG. 5. The frequency of LEO phonons estimated from folding the  $B$  zone as a function of the inverse square root of atomic mass  $M$  as  $1/(M)^{1/2}$ , in which  $M$  is the mobile ion mass for a SIC and heavier ion mass for group II-VI compounds. Lines A and B are drawn through the SIC's and group II-VI non-SIC's, respectively.

The extremely small temperature dependence of the frequency of the LE mode observed<sup>68</sup> is also understood from the property of the LEO phonon, since a negative value of the Grüneisen-mode parameter gives a positive shift that cancels the negative shift due to the anharmonic phonon-phonon interaction.

The proportionality of  $(M_{\text{mo}})^{-1/2}$  to the  $\omega_{\text{LE}}$  value, where  $M_{\text{mo}}$  is a mobile ion mass, has been previously reported.<sup>68</sup> This proportionality is one of characteristics of the LEO phonon, as shown from the frequency of the transverse ZEA phonon for a linear chain with two kinds of atoms.<sup>32</sup> It leads to the proportionality  $(M)^{-1/2}$ , where  $M$  is the heavier atomic mass. The transverse ZEA phonon of  $\text{CuCl}$ ,  $\text{Cu}_2\text{S}$ , and  $\text{Ag}_2\text{X}$  ( $X=\text{S}, \text{Se}$ ) must exhibit the proportionality  $(M_{\text{mo}})^{-1/2}$  since the heavier ion is equal to the mobile ion. On the other hand, in  $\text{Cu}_2\text{Se}$ ,  $\text{Ag}_2\text{Te}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{AgI}$ , etc. the heavier atom is not a mobile ion but the magnitude of  $M_{\text{mo}}$  is within 10% of the heavier atomic mass. Therefore, the value of  $\omega_{\text{LEO}}$  must be approximately proportional to  $(M_{\text{mo}})^{-1/2}$ . Indeed, predicted values for WZ-type  $\text{CuX}$  ( $X=\text{Br}, \text{I}$ ) are slightly larger than the observed  $\omega_{\text{LEO}}$  and are independent of the anion mass.<sup>36–39</sup>

Estimated values as a function of mobile-ion atomic mass are shown in Fig. 5, where  $M$  of group II-VI compounds is the heavier atomic mass. Two linear relations are shown by line A for SIC's and by line B for non-SIC's. Since the slope of line A is lower than that of line B, a weak interionic force for SIC's is suggested. The cause of this weakness may be related to the ionic character of SIC's since those take higher ionicity than that of group II-VI compounds.

### B. Relationship between the LEO phonon and crystal structure

Since the LEO phonon is induced from the specific crystal structure that has the plural units under similar atomic arrangement appearing just below  $T_{c1}$ , we can indicate a close relationship between the LEO phonon and the SI-conduction phase.

In some of the mobile ion-type binary SIC's, the transition to the SI-conduction phase arises at a higher transition

temperature  $T_{c2}$ , as listed in Table IV, and the LEO phonon exists at a temperature below  $T_{c2}$ , as listed in Table III. For example, the crystal structure of AgI changes at  $T_{c1}$  (=410 K) and the SI-conduction phase appears at  $T_{c2}$  (=419 K).<sup>71</sup> The LEO phonon appears at a temperature between  $T_{c1}$  and  $T_{c2}$ . Another example is the mobile ion-type SIC  $\text{Ag}_2\text{S}$ . Below  $T_{c2}$ , the unit cell involves plural units with similar atomic arrangements,<sup>72</sup> and the LEO phonon appears.<sup>73</sup> On the other hand, the SI-conduction phase appears above  $T_{c2}$ . From these behaviors, we can suggest the presence of the SI-conduction phase based on the LEO phonon.

This relation is also found in ternary compounds as seen in Table IV. In  $M\text{Ag}_4\text{I}_5$  ( $M=\text{Rb}, \text{K}$ ) and  $\text{Ag}_3\text{SX}$  ( $X=\text{I}, \text{Br}$ ), the LEO phonon and the SI-conduction phase appear at temperatures below and above  $T_{c1}$ , respectively. In defect-type chalcopyrites  $M_2\text{NX}_4$  ( $M=\text{Ag}, \text{Cu}$ ;  $N=\text{Hg}, \text{Cd}$ ;  $X=\text{S}, \text{Se}$ ), plural units in the unit cell have similar atomic arrangements and the LEO phonon exists at a temperature below  $T_{c1}$ . Then the SI-conduction phase appears at a temperature above  $T_{c1}$ .

On the other hand, the SIC's having a high transition temperature do not contain the LEO phonon, as seen in Table IV.<sup>74</sup> For example, the normal phase of defect-type binary SIC,  $MY_2$  ( $M=\text{Ca}, \text{Ba}, \text{Sr}$ ;  $Y=\text{F}$  or  $\text{Cl}$ ), has plural units but the atomic arrangements of those units are not the same. Therefore the rule for the  $B$ -zone folding, described in Sec. V, cannot be satisfied and so the LEO phonon is not induced, as seen experimentally.<sup>74-76</sup> In  $MY_2$ , if many defects are produced near  $T_c$ , the LEO phonon may arise since plural units with similar atomic arrangements can be induced by the defects.

The cause of the absence of the SI-conduction phase in  $\text{CuF}$  and  $\text{AgX}$  ( $X=\text{F}, \text{Cl}, \text{Br}$ ) is directly related to the non-existence of the LEO phonon. Since the atomic arrangement in the unit cell of the crystal is microscopically isotropic, it does not give the long-range periodicity. Therefore it does not satisfy the condition for the folding of the  $B$  zone and no LEO phonon appears.

From these results, we can conclude that the transition of the SI-conduction phase at low temperature  $T_{c1}$  is related to the specific crystal structure, satisfying the rule for the existence of the LEO phonon.

### C. Role of LEO phonon on mobile defects

The contribution of the LEO phonon to the motion of mobile ions is supported by the success of the classification for SIC's, based on the vibrational amplitude,<sup>14</sup> and by several suggestions, for example, the significant role of the edgewise optical phonon on the high ionic conduction of AgI,<sup>34</sup> the large amplitude for the  $c$  direction in  $(\text{C}_5\text{H}_5\text{NH})\text{Ag}_4\text{I}_5$ ,<sup>77</sup> and the effective contribution of the optical phonon to the increase of defects.<sup>21</sup> Further, it may be supported by the empirical relationships between the  $\omega_{\text{LEO}}$  and the activation energy  $E_{\text{ac}}$ ,<sup>14</sup> and between the phonon frequency and  $T_c$  value.<sup>7</sup> The role of the acoustic phonon for the self-diffusion of bcc metal also supports this.<sup>78</sup> These results strongly suggest that the LEO phonon is closely connected to high ionic conduction.

The importance of the zone-center optical phonon for high ionic conduction can be clarified by noticing the vibration phase of the LEO phonon. The zone-center optical phonon exhibits long wavelength, implying the same phase, and vibrates the ions for the same direction through the nearest-neighbor cells and provides an appropriate path for the motion of defects, assisting the carrying of ions to more distant neighbors. On the other hand, ZEA phonons exhibit short wavelength, implying an inverse phase within short range, and vibrates the ions for the opposite direction. It disturbs the smooth motion of ions to more distant neighbors. In addition, we know that the shear mode that characterizes the LEO phonon may be significant for the jump of mobile ions.<sup>34</sup>

### D. Equivalence of LEO phonon to low-energy mode

The properties of the LEO phonon can be used to interpret the small value of  $\omega_{\text{LE}}$ , the small dispersion, the independence of  $\omega_{\text{LE}}$  from some kinds of constituent atoms, the proportionality of  $\omega_{\text{LE}}$  to  $(M_{\text{mo}})^{-1/2}$ , and the decrease of  $\omega_{\text{LE}}$  with increasing temperature<sup>40,68</sup> and pressure.<sup>67,69,70</sup> These results confirm the equivalence of the LEO phonon to the LE mode.

The energy for the LEO phonon and LE mode is listed in Table III,<sup>25,76,79,80</sup> together with the value of  $\omega_{\text{LEO}}$  estimated from the folding of the  $B$  zone. The  $\omega_{\text{LE}}(\text{calc.})$  values for the proposed models exhibit considerable scattering and are model dependent. However, the values due to the  $B$ -zone folding are in good agreement with the observed values except in the case of (Ag)  $\beta$ -alumina. This result suggests that the discrepancy in the proposed model is because it is assumed that the ionic plasmon is only due to mobile ions, and does not account for the coupling with the phonon mode arising from the cage ion.

## VIII. SUMMARY

The origin of the low-energy mode in binary and ternary compounds of SIC's was shown to be the zone-center optical phonon originating from the ZEA phonon. By folding the  $B$  zone at a point between the zone edge and the center of the  $B$  zone, the phonon distribution of the  $\beta$  phase in AgI was obtained from that of the  $\gamma$  phase.

Characteristic properties of the LEO phonon were interpreted by the procedure described in Sec. V. The frequency of the LEO phonon was shown to have a negative pressure dependence, an extremely small temperature dependence, and was proportional to the inverse square root of the mobile ion mass  $(M_{\text{mo}})^{-1/2}$ . These dependencies are the same as those of the LE mode and were understood with respect to the property of the ZEA phonon. The appearance of numerous bands at separated frequencies at low temperature was also explained by folding the  $B$  zone.

The close relationship between the LEO phonon and SI-conduction phase was because the specific crystal structure satisfying the rule for the  $B$ -zone folding and the same phase of vibration through the near-neighbor ions.

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