Piezoelectric scattering of optical polaron in halide perovskites

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For the intrinsic carriers of MAPbBr$_3$, the temperature $T$ dependent mobility $\mu(T)$ of behaves like $\mu \propto T^{1/2}$ in piezoelectric tetragonal phase, $\mu \propto T^{-1.4}$ in non-piezoelectric cubic phase. But for the photo-generated carriers in other halide perovskites ABX$_3$, $\mu \propto T^{-3/2}$ behavior is typical. Due to the strong interaction of carrier with longitudinal optical phonon, in ABX$_3$ the carriers mainly exist as optical polarons. The softness of ABX$_3$ renders it without inversion center in tetragonal phase, which allows piezoelectric effect at low carrier concentration. The variations of $\mu(T)$ behavior results from (1) the wave vector dependence of the piezoelectric interaction of polarons with acoustic phonons is different from that of ordinary polaron-acoustic phonon interaction; (2) the residual interaction of polaron with 2 longitudinal optical phonons can be ignored at low temperature, but is important at higher temperature; and (3) the concentration of intrinsic carriers is determined by temperature, while the concentration of photo-generated carriers is determined by the incident flux of photons.

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I. INTRODUCTION

In the photovoltaic application of halide perovskites ABX$_3$ (A=MA$^+$, BA$^+$, Cs$^+$; B= Pb$^{2+}$, Sn$^{2+}$; X=I$^-$, Br$^-$, Cl$^-$), one of the key parameters is the temperature $T$ dependent carrier mobility $\mu(T)$ \cite{1,2}. ABX$_3$ is an ionic crystal, due to the strong interaction of electron (hole) with longitudinal optical (LO) phonons, electrons (holes) mainly exist as optical electronic (hole) polarons \cite{4-10}. For the photo-generated carriers in non-piezoelectric phase, $\mu(T) \propto T^{-3/2}$ is typical \cite{11-13}, which results from: (1) the screening to the interactions of polaron with other elementary excitations is primarily caused by the displacements of ions \cite{14,16}; (2) the change in the momentum distribution function of polaron is dominated by the 1-longitudinal acoustic (LA) phonons emission or absorption; and (3) the concentration $n_e$ of electrons (holes) is fixed by the incident flux of photons \cite{10}. Recently, for the intrinsic carriers in MAPbBr$_3$, a different behavior is observed: $\mu(T) \propto T^{-1/2}$ for tetragonal phase $160K < T < 236K$; and $\mu(T) \propto T^{-1.4}$ for cubic phase $236K < T < 280K$ \cite{13}. It is compelling to investigate: (1) the reasons lead to different $\mu(T)$ behaviors in above two temperature regimes; and (2) why the transport behavior of intrinsic carriers in MAPbBr$_3$ is different to that of the photo-generated carriers in other halide perovskites.

The outline of this work is as following: in Sec.\textbf{II} we first determine the existing condition of piezoelectric effect in MAPbBr$_3$. The appearance of piezoelectric effect in a superparaelectric state makes the polarization-strain tensor and dielectric function increase with the decrease of temperature. In Sec.\textbf{III}, we contrast the piezoelectric coupling $H_{\text{pie}}$ of electron with acoustic phonon in piezoelectric phase and the ordinary electron-acoustic phonon interaction $H_{\text{e-Aph}}$ in non-piezoelectric phase. In Sec.\textbf{IV}, by comparing the strengths of $H_{\text{pie}}$ and $H_{\text{e-Aph}}$ with the strength of electron-LO phonon interaction $H_{\text{e-LO}}$, we argue that the electrons (holes) mainly exist as optical polaron in both piezoelectric tetragonal phase and non-piezoelectric cubic phase. In Sec.\textbf{V} we determine the dominant interaction(s) controlling charge transport by comparing the residual 2-LO phonon interaction $H_{\text{P-LO}}$ of polaron with the piezoelectric polaron-acoustic phonon interaction $H_{\text{P-pie}}$ in piezoelectric phase, and with the ordinary polaron-LA phonon interaction $H_{\text{P-LA}}$ in non-piezoelectric phase. In Sec.\textbf{VI} by analyzing the collision integral in Boltzmann equation, we find that the $\mu(T) \propto T^{-1/2}$ behavior in tetragonal phase of results from two reasons: (1) each term in $H_{\text{P-pie}}$ is proportional to $k^{-1/2}$, where $k=|\mathbf{k}|$, $\mathbf{k}$ is the wave vector of acoustic phonon; and (2) the equilibrium distribution $f_{\text{eq}}$ of polarons is given by $\exp(-\hbar^2 k^2/2m_p k_B T)$ \cite{16}, where $p=|\mathbf{p}|$, $\mathbf{p}$ is wave vector of polaron. In Sec.\textbf{VII} we show that for intrinsic carriers, $H_{\text{P-LA}}$ leads to $\mu(T) \propto T^{-1}$, $H_{\text{P-LO}}$ leads to $\mu(T) \propto T^{-3/2}$. Finally, we explain why $\mu(T)$ for the intrinsic carriers is different to $\mu(T)$ for the photo-generated carriers.

II. INTERPLAY OF PIEZOELECTRIC AND SUPERPARAELECTRIC

From the phase diagram of MAPbBr$_3$, we induct the existing temperature range of piezoelectricity. Above 236K, MAPbBr$_3$ is in cubic phase \cite{14}, which cannot be statically piezoelectric due to the existence of inversion center \cite{17}. For 149K $< T < 236K$, MAPbBr$_3$ is in tetragonal phase; below 149K, orthorhombic phase \cite{14}. Because of the softness of MAPbBr$_3$, even in tetragonal phase inversion center cannot exist. Both tetragonal and orthorhombic phases of MAPbBr$_3$ lack of inversion center, which is a necessary condition to be a piezoelectrics \cite{17}.

The temperature dependent dielectric function \cite{14} help us to surmise the superparaelectricity and ferro-
electricity. Denote $\varepsilon(\omega, T)$ as the frequency $\omega$ and temperature $T$ dependent dielectric function. Above 149K, the observed $\varepsilon(0, T)$ can be described by Curie–Weiss law, i.e. MAPbBr$_3$ is in a superparaelectric phase \cite{14}; below 149K, $\varepsilon(0, T < 149K) \approx \varepsilon_\infty$, the optical dielectric constant caused by bound electrons \cite{14}. The above facts indicates that: (1) If MAPbBr$_3$ continued staying in tetragonal phase below 149K rather than become an orthorhombic phase, it would be in a ferroelectric phase below a critical temperature $T_c$. $T_c$ is a very small positive number; (2) the rigid orthorhombic phase greatly limited the displacements of B$^{2+}$ and X$^{-}$ ions, only the positive bound electrons cause screening, ferroelectric phase cannot be realized even at $T = 0$K. Because piezoelectric effect requires shifts of ions, it is also impaired in orthorhombic phase. Summing up above discussion, for 149K$< T < 236$K, tetragonal MAPbBr$_3$ is both piezoelectric and superparaelectric.

When a material is in a state which is both piezoelectric and superparaelectric, its dielectric function and polarization-strain tensor has unusual temperature dependence. Denote $\Phi$ as the thermodynamic potential density with electric field and stress tensor as independent variables. Then for $T > T_c$, one has \cite{17}:

$$
\Phi = \Phi_0 + A(T - T_c)P_z^2/\epsilon_0 + BP^4 - \Lambda P_z \sigma_{xy}
$$

$$
- \mu(P)^2 \sigma_{xy} - E_z P_z - \frac{\epsilon_0}{2} E_z^2,
$$

(1)

where $P_z$ is the z-component of polarization vector, $E_z$ is the external electric field, $A$ is the piezoelectric coefficient, $\sigma_{xy}$ is the xy-component of stress tensor, $\mu(P)$ is the modulus for constant polarization $P_z$, $A$ and $B$ are usual expansion coefficients of free energy for paraelectric-ferroelectric transition. Using $\partial \Phi / \partial P_z = 0$ and neglecting $P_z^3$ term, the equilibrium polarization is \cite{17}:

$$
P_z = \frac{\epsilon_0 (E_z + \Lambda \sigma_{xy})}{2A(T - T_c)}.
$$

(2)

In a piezoelectric material, the polarization-strain tensor $\Xi_{\alpha\beta\gamma}$ is defined by $P_z = \Xi_{\alpha\beta\gamma} u_{\alpha\beta\gamma}$, where $u_{\alpha\beta\gamma}$ is the strain tensor, $\alpha$, $\beta$, $\gamma = x, y, z$. The strain $u_{\alpha\beta\gamma}$ of a material specifies the configurations of atoms, the later directly relates to the polarization $P_z$ caused by the displacements of atoms. Therefore $\Xi_{\alpha\beta\gamma}$ is an inquityan quantity. The polarization-stress tensor $\Gamma_{\alpha\beta\gamma}$ is defined by $P_z = \Gamma_{\alpha\beta\gamma} \sigma_{\alpha\beta\gamma}$, where $\sigma_{\alpha\beta\gamma}$ is the stress tensor \cite{18}. $\sigma_{\alpha\beta\gamma}$ relates to $u_{\alpha\beta\gamma}$ by $u_{\alpha\beta\gamma} = c_{\alpha\beta\gamma} \delta_{\alpha\beta\gamma}$, where $c_{\alpha\beta\gamma}$ is the elastic constant tensor. Repeated indices are implicitly summed over. One can easily see the relation between two piezoelectric coefficients:

$$
\Xi_{\alpha\beta\gamma} = \Gamma_{\gamma\alpha\beta} e_{\alpha\beta\gamma},
$$

(3)

or

$$
\Gamma_{\gamma\alpha\beta} = \Xi_{\alpha\beta\gamma} (e^{-1})_{\alpha\beta\gamma}.
$$

(4)

where $\xi, \eta = x, y, z$. \cite{19}. Eq. (11) tell us that softer materials like halide perovskites have a larger electrical response to stress. Later we will suppress the indices of tensor if not cause confusion. From Eq. (12), one has $\Gamma_{\gamma\alpha\beta} = \epsilon_0 \Lambda [2A(T - T_c)]^{-1}$. By means of Eq. (3), the polarization-strain tensor is

$$
\Xi = \epsilon_0 \Lambda [2A(T - T_c)]^{-1}.
$$

(5)

Comparing to factor $(T - T_c)^{-1}$ in Eq. (5), the temperature dependence of $c_{\alpha\beta\gamma}$ is very weak \cite{20}, we shall view $c\Lambda$ as a temperature-independent constant.

For $T > 236$K, MAPbBr$_3$ is still superparaelectric but no longer piezoelectric. $\Phi$ is simplified to \cite{17}:

$$
\Phi = \Phi_0 + A(T - T_c)P_z^2/\epsilon_0 + BP^4 - \frac{\epsilon_0}{2} E_z^2.
$$

(6)

Eqs. (10) imply that for both tetragonal phase and cubic phase,

$$
\varepsilon(\omega, T) = \varepsilon_\infty + \frac{1}{2A(T - T_c)}.
$$

(7)

Eq. (7) could reproduce the observed $\varepsilon(0, T)$ \cite{14}. The form of $\varepsilon(\omega, T)$ is the same for both the piezoelectric tetragonal phase and non-piezoelectric cubic phase. For a halide perovskite not in orthorhombic phase \cite{14}, the screening caused by bound electrons is much smaller than that caused by the displacements of ions, i.e. $\varepsilon_\infty \ll [2A(T - T_c)]^{-1}$, one has

$$
\varepsilon(\omega, T) \approx \frac{1}{2A(T - T_c)}.
$$

(8)

\section{III. ELECTRON-Acoustic PHONON INTERACTION}

The piezoelectric carrier-acoustic phonon interaction is different to the ordinary carrier-acoustic phonon interaction in a non-piezoelectric phase. When a material is piezoelectric, the interaction $H_{\text{e-pie}}$ of an electron (hole) at position $x$ with the acoustic phonons is \cite{18}:

$$
H_{\text{e-pie}} = \sum_{s,k} V_{\text{pie}}^{s}\left(\tilde{a}_{sk} e^{i k \cdot x} + \tilde{a}_{sk}^\dagger e^{-i k \cdot x}\right),
$$

(9)

where

$$
V_{\text{pie}}^{s} = \frac{q Z_s e_s(k)}{2e_0 \sqrt{2 M c_s k}},
$$

(10)

is the coupling energy of electron (hole) with acoustic phonon $|s, k\rangle$ and $\tilde{a}_{sk}$ is the annihilation operator for $|s, k\rangle$ phonon. Denote $k_s$ as $s$th component of wave vector $k$. $\Xi_s = \hat{k}_s \Xi \hat{k}_s$ is the reduced
polarization-strain coefficient, $\tilde{k}_a = k_a/k$. $\varpi = k_a \varepsilon_{\alpha \beta} k_{\beta}$ is the reduced dielectric function. Eq. (9) shows that: (a) all three acoustic branches contribute to $H_{e-pie}$; (b) $V_{k_s}^\text{pie} \propto k^{-1/2}$. The dielectric property of MAPbBr$_3$ is not very anisotropic, we may approximate $\varpi$ with Eqs. (7, 8). Noticing Eqs. (4, 8), we can see that each term in $H_{e-pie}$ is proportional to $[1 + 2A(T - T_c)\varepsilon_{\infty}]^{-1} \approx 1$, a very weak monotonically decreasing function of $T$

For a non-piezoelectric material, the interaction $H_{e-ph}$ of a carrier at position $x$ with acoustic phonons is

$$H_{e-ph} = \sum_{sk} \frac{V_{e-Aph}^{sk}}{\sqrt{N}} (a_{sk} e^{i k \cdot x} + a_{sk}^\dagger e^{-i k \cdot x}),$$

where

$$V_{e-Aph}^{sk} = \frac{\hbar}{2c_s \varepsilon (c_s k, T) k^2 \varepsilon_0 \Omega / M_k},$$

$M_k$ and $c_s$ are the mass and effective nuclear charge of the $k$th atomic core in a primitive cell, $r_s$ is the position vector of the $k$th atom relative to the center-of-mass of a primitive cell, $e_{\varpi}^s(k)$ is the polarization vector of the $k$th atom for $|sk\rangle$ phonon. Eq. (11) shows that (a) at least in the long wave limit, only the longitudinal acoustic (LA) phonon contribute to $H_{e-Aph}$, later we will denote it as $H_{e-LA}$; (b) Each term in $H_{e-ph}$ is proportional to $k^{-3/2}$.

Noticing Eqs. (4, 8), we can see that each term in $H_{e-Aph}$ is proportional to $2A(T - T_c)$, a monotonically increasing function of $T$.

IV. OPTICAL POLARONS AS THE MAIN CARRIERS

Assuming carriers are bare electrons (holes), a calculation shows that piezoelectric scattering leads to $\mu \propto T^{-1}$ [22], which is not fit the observed $\mu \propto T^{-1/2}$ in the piezoelectric tetragonal phase of MAPbBr$_3$ [13]. Thus, the main carriers in ABX$_3$ cannot be bare electrons (holes).

Let us show that in ABX$_3$ the electrons (holes) mainly exist as optical polarons, neither piezoelectric polarons nor piezoelectric-optical polarons. In any ionic crystal, piezoelectric or non-piezoelectric, the interaction $H_{e-LO}$ of electron (hole) with a branch of longitudinal optical (LO) phonons is [23]

$$H_{e-LO} = \sum_k \frac{V_k^o}{\sqrt{N}} (a_{k0} e^{i k \cdot x} + a_{k0}^\dagger e^{-i k \cdot x}),$$

where

$$V_k^o = i\hbar \frac{\Omega_k^{\varpi}}{2 \varepsilon_0 \Omega} \left( \frac{1}{\varepsilon_{\infty}} - 1 \right)^{1/2} \frac{k \cdot e_{k0}}{k^2},$$

is the coupling energy of electron (hole) with LO phonon in optical mode $|k0\rangle$, $k$ is the wave vector of phonon, $k = |k|$, $e_{k0}$ is the polarization vector of $|k0\rangle$, $a_{k0}$ is annihilation operator of $|k0\rangle$ phonon, $\omega_{LO}$ is the frequency of LO phonon. $\varepsilon_0$ is the static dielectric constant, $q$ is the charge of carrier, $\Omega$ is the volume of a primitive cell. $N$ is the number of primitive cells in a sample with volume $V = N\Omega$. $H_{e-LO}$ is not sensitive to use cubic or tetragonal lattice. Later we will use the primitive cubic lattice, then $\Omega = a_x^3$, where $a_x$ is the length of basis vector along $x$-direction. One can see from Eq. (14) that $V_k^o \propto k^{-1}$.

We estimate the piezoelectric coupling energy in Eq. (9). The bulk modulus of MAPbBr$_3$ is 20GPa, speed of longitudinal sound is $c_s \approx 2000$ m/s [24]. $\Gamma \approx 31.4 \times 10^{-12}$ C·N$^{-1}$ [23], $\varepsilon_0 = 70$, $\varepsilon_{\infty} = 6.5$. $a_x = 6.3$, $\hbar \omega_{LO} \approx 15.3$ meV [26]. Denote $k_0 = \pi/a_x$ as the wave vector at the boundary of Brillouin zone. Then, $V_k^o = (h/2Mc_s k_b)^{1/2} q_{e}/2\varepsilon_0 \approx 13.9$ meV, and $V_k^o \approx 55.7$ meV.

Since in tetragonal phase of MAPbBr$_3$, $H_{e-pie} < H_{e-LO}$, piezoelectric polaron or piezoelectric-optical polaron do not form [13, 23, 28]. In both tetragonal and cubic phase, $H_{e-LO} > \hbar \omega_{LO}$, $H_{e-pie}$ and $H_{e-Aph}$, then the electrons (holes) mainly exist as optical polarons [13, 10] in both phases.

V. RESIDUAL INTERACTIONS OF POLARON WITH PHONONS

We enumerate various interactions of polaron with other elementary excitations. After the polaron transformation, the 1-LO phonon interaction [13] disappeared, and the residual interaction $H_{p-LO}$ of polaron with LO phonons is [28]

$$H_{p-LO} = \sum_{kk'} O_{-k'k}(a_{k'0}^\dagger + a_{-k'0}^\dagger)(a_{k0} + a_{-k0}) + \cdots ,$$

where

$$O_{-k'k} = V_{k}^o V_{k'}^o \sum_{n \neq 0} J^{n}_{-k'0} J^{n}_{k0} \delta_n E_n - E_0,$$

$E_n$ and $\varphi_n$ are the eigen values and eigen wave function of the polaron Hamiltonian $H_p$, $J^{n}_{k0} = \int d^3x \varphi^*_n(x) e^{ik' \cdot x} \varphi_n(x)$ is a parameter describing the internal motion of carrier in the potential well induced by phonons, the dependence on $k'$ is weak [28, 29].

In piezoelectric tetragonal phase, after the formation of optical polaron, $H_{e-pie}$ becomes the piezoelectric interaction $H_{p-pie}$ of polaron with acoustic phonons:

$$H_{p-pie} = \sum_{sk} V^{p-pie}_{ks} (a_{sk} e^{i k \cdot x} + a_{sk}^\dagger e^{-i k \cdot x}),$$

where

$$V^{p-pie}_{ks} = \frac{q \varepsilon_0 e_{k0}^s(k)}{2 \varepsilon_0} \sqrt{\frac{\hbar}{2Mc_s k}},$$

(18)
Because the charge of electronic (hole) polaron is same as the charge of an electron (hole), Eqs. (17,18) have the same form as Eqs. (11,12). Eqs. (14,16,18) indicates that $H_{P,\text{pie}}$ is stronger than $H_{P,\text{LO}}$.

In non-piezoelectric cubic phase, after the formation of polaron, $H_{c,\text{LA}}$ becomes the polaron-LA phonon interaction $H_{P,\text{LA}}$:

$$H_{P,\text{LA}} = \sum_{\mathbf{k}} \frac{V_{\text{LA}}^{\text{p}}}{\sqrt{N}} (a_{\text{kLA}}^\dagger e^{i\mathbf{k}\cdot\mathbf{x}} + a_{\text{kLA}} e^{i\mathbf{k}\cdot\mathbf{x}}) \tag{19}$$

where

$$V_{\text{LA}}^{\text{p}} = \sqrt{\frac{\hbar}{2m_e^*}} \sum_{\mathbf{r},\mathbf{n}} e^{i\mathbf{n}\cdot\mathbf{r}} \langle \mathbf{n} | e^{-\mathbf{r}^2/\sigma} \mathbf{e}^{i\mathbf{k}\cdot\mathbf{r}} \rangle \tag{20}$$

Eqs. (19-20) have the same form as Eqs. (11,12). According to Eq. (8), the screening becomes weaker at higher temperature. Thus, in cubic phase, $H_{P,\text{LA}}$ is comparable to $H_{P,\text{LO}}$.

By means of golden rule, one can show that for $n_e < 10^{23} \text{cm}^{-3}$ and moderate defect concentration ($\lesssim 10^{20} \text{cm}^{-3}$), the scattering probabilities per unit time produced by the Coulomb interaction between polarons and by the interaction of polaron with defects are much smaller than those caused by $H_{P,\text{LO}}$ and by the interaction of polaron with acoustic phonons [10]. For the aim of calculating mobility, we can ignore the Coulomb interaction between polarons and the interaction of polaron with defects [3,7].

**VI. MOBILITY IN PIEZOELECTRIC PHASE**

If a polaron does not interact with other objects, its state can be characterized by wave vector $\mathbf{p}$ [23]. Denote $f_\mathbf{p}$ as the distribution function of polaron. Each interaction of polaron produces a change in distribution function $f_\mathbf{p}$, corresponds to an collision integral in Boltzmann equation [30]. If there are $N$ types of interactions of polaron, the total change rate $\nu(T)$ of $f_\mathbf{p}$ is $\nu(T) = \sum_{j=1}^{N} \nu_j(T)$, where $\nu_j(T)$ is the change rate of $f_\mathbf{p}$ caused by the $j$th interaction. The mobility $\mu(T)$ of polaron is determined by: $\mu(T) = q/m_n \nu(T)$, where $q$ and $m_n$ are the charge and effective mass of polaron [22,30].

In tetragonal piezoelectric phase, the charge transport of polaron is controlled by $H_{P,\text{pie}}$. The rate $\nu_{\text{pie}} = (\partial f_\mathbf{p}/\partial t)_{\text{pie}}$ of change in distribution function $f_\mathbf{p}$ of polaron with wave vector $\mathbf{p}$ caused by $H_{P,\text{pie}}$ is [31]

$$\frac{\partial f_\mathbf{p}}{\partial t} \bigg|_{\text{pie}} = -\sum_{\mathbf{k}} \frac{\partial N_0(h_c \kappa k)}{\partial h_c k} \left[ f_0(\mathbf{p}') - f_0(\mathbf{p}) \right] \tag{21}$$

$$\{ w(\mathbf{p}', \mathbf{p}; \mathbf{k}) (\varphi_{\mathbf{p}'} - \varphi_{\mathbf{p}} + \chi_{\mathbf{p}k}) \delta(E_\mathbf{p} - E_{\mathbf{p}'} - h_c k)$$

$$- w(\mathbf{p}', \mathbf{p}; \mathbf{k}) (\varphi_{\mathbf{p}'} - \varphi_{\mathbf{p}} - \chi_{\mathbf{p}k}) \delta(E_\mathbf{p} - E_{\mathbf{p}'} + h_c k) \}$$

where $f_0$ and $N_0$ are the equilibrium distribution functions at temperature $T$ for polaron and phonons, $E_\mathbf{p} = \hbar^2 p^2/2m_p$ is the kinetic energy of polaron, $m_p$ is the mass of polaron. $\varphi$ and $\chi$ describe the deviations of $f_0$ and $N_0$ from equilibrium

$$f_\mathbf{p} - f_0(\mathbf{p}) = -\frac{\partial f_0(E_\mathbf{p})}{\partial E_\mathbf{p}} \varphi_{\mathbf{p}}, \tag{22}$$

and

$$N_{\mathbf{p}k} - N_0(\mathbf{p}k) = -\frac{\partial N_0(h_c \kappa k)}{\partial h_c k} \chi_{\mathbf{p}k}. \tag{23}$$

At temperature $T$, the characteristic energies $\varphi_{\mathbf{p}}$ and $\chi_{\mathbf{p}k}$ are order of $k_B T$, then $\varphi_{\mathbf{p}} + \chi_{\mathbf{p}k} \sim k_B T$ [19,30]. Because the density $n_e$ of polarons gas is rare, polaron momentum is much smaller than $k_B = \pi/a_x$. One can neglect reciprocal processes. $\mathbf{p}' = \mathbf{p} + \mathbf{k}$ is implied in Eq. (21), then

$$\delta(E_\mathbf{p} - E_{\mathbf{p}'} + h_c k) \tag{24}$$

or

$$\frac{2\pi}{\hbar} |\langle \mathbf{p}', \mathbf{sk} | H_{P,\text{pie}} | \mathbf{p} \rangle|^2 = w(\mathbf{p}', \mathbf{sk}; \mathbf{p})(N_{\mathbf{p}k} + 1), \tag{25}$$

$$\frac{2\pi}{\hbar} |\langle \mathbf{p}', \mathbf{sk} | H_{P,\text{pie}} | \mathbf{p} \rangle|^2 = w(\mathbf{p}', \mathbf{sk}; \mathbf{p})N_{\mathbf{p}k}, \tag{26}$$

the occupation number and energy consideration delta function are factored out from the transition probability. Using Eqs. (18-26), one has

$$w \sim \frac{2\pi}{\hbar} \frac{2}{N M_c k^2} \frac{q e^2 \kappa^2}{2 \pi \epsilon_0} \tag{27}$$

$$\sim \frac{2\pi}{\hbar} \frac{2}{N M_c k^2} \frac{q e^2 \kappa^2}{2 \pi \epsilon_0} \tag{28}$$

The probability coefficient $w(\mathbf{p}', \mathbf{k}; \mathbf{p})$ is defined by

Take the direction of wave vector $\mathbf{p}$ of the initial state of polaron as the polar axis, then $\sum_k \rightarrow (2\pi)^{-3} \sum k^2 dkd \cos \theta d\phi$, where $(\theta, \phi)$ are the polar and azimuth angles of $\mathbf{k}$ relative to $\mathbf{p}$. In halide perovskites, even $h_c k_0 = 75 K \ll k_B T$ in experimental temperature range 160-280K. Since $k \leq k_0$, then for all $\mathbf{k}$,

$$\frac{\partial N_0(h_c \kappa k)}{\partial h_c k} \sim \frac{k_B T}{(h_c k)^2} \tag{28}$$

For the thermal generated intrinsic carriers, the density $n_e$ of electrons (i.e. polarons) is temperature dependent [16]. Because $n_e$ is small, the polaron gas is non-degenerate, the equilibrium distribution $f_0$ of polaron with wave vector $\mathbf{p}$ is [16]

$$f_0 \approx \exp(-\hbar^2 p^2/2m_p k_B T), \tag{29}$$
where $m_p$ is the mass of polaron. The delta function in Eq. (21) requires $E_{p'} = E_p + h c_s k$, then

$$f_0(p') - f_0(p) = \frac{\partial f_0(E_p)}{\partial E_p} (E_{p'} - E_p)$$

$$\sim \frac{h c_s k}{2 m_p k_B T} \exp(-\frac{h^2 c_s^2}{2 m_p k_B T}).$$

(30)

Substitute Eqs. (22, 23, 24, 27, 28, 30) into Eq. (21), and carry out the momentum integral, one obtains

$$\nu_{p-pie} = \frac{e^{-3/2} \sqrt{3 m_p k_B T}}{2 \pi \rho}$$

(31)

$$\sum s \frac{q c A}{h c_s} \ln \frac{\sqrt{3 m_p k_B T - m_p c_s}}{\sqrt{3 m_p k_B T + m_p c_s}},$$

where $c$ is the base of natural logarithm, $\rho = M/\Omega$ is the density of halide perovskites. In derive Eq. (31), energy equipartition theorem has been used: the average momentum $\hbar p$ of polaron is taken as $\hbar p = \sqrt{3 m_p k_B T}$. The logarithm factor in Eq. (31) only weakly depends on temperature, therefore $\mu \propto T^{-1/2}$ in piezoelectric tetragonal phase. One can see that two critical ingredients for intrinsic carriers is Eq. (29). The piezoelectric electron-phonon interaction has been discussed with deformation potential approximation in which $H_{pie} \propto k^{-1}$ [31] in contrast to Eq. (11). The square of transition element $|M(k, k')|^2 = E_1^2 k_B T/2 c$ was used to derive $\mu \propto T^{-1/2}$, where $c$ is elastic constant, $E_1$ is the deformation potential energy [31]. The key assumption behind this derivation is that the polarization-strain tensor does not depend on temperature in contrast to Eq. (5). A future knowledge of $\Xi(T)$ in halide perovskite could resolve which reasoning is more plausible.

In Fig. 1(a) we compare the observed mobility for intrinsic carriers in tetragonal phase of MAPbBr$_3$ with that estimated from Eq. (31). Due to lack of components of tensor $\Xi_{\nu \rho}$, in the calculation, elastic modulus $c$ taken as 20GPa [24], $\Gamma \approx 31.4 \times 10^{-12} C \cdot N^{-1}$ [23], $\Xi = 6.28 \times 10^{-12} C \cdot m^{-2}$, $m_p = 3.8 m_e$, $c_s = 2000 m/s$ are used, where $m$ is mass of electron. The agreement is reasonable well. For the intrinsic carriers in MAPbI$_3$, $\mu \propto T^{-0.42}$ has been observed at $50 < T < 150K$ [32], it seems indicate that the orthorhombic phase is also piezoelectric.

VII. MOBILITY IN NON-PIEZOELECTRIC PHASE

In Sec.V we noticed that $H_{p-LO}$ is comparable to $H_{p-LA}$, both contribute to $\partial f_p/\partial t$ significantly. By similar procedure deriving Eq. (31), the change rate

$$\nu_{p-LA} = (\partial f_p/\partial t)_{p-LA}$$

of distribution function $f_p$ of polaron caused by $H_{p-LA}$ can be obtained:

$$\nu_{p-LA} = \frac{e^{-3/2} k_B T^3 A^2 m_p^2}{2 \pi c (3 m_p k_B T - (m_p c_s)^2)^3/2}$$

where an average over all $k$ points is taken in the last factor. If $H_{p-LA}$ was the solely interaction changing $f_p$, Eq. (32) would imply $\mu(T) = q/m_p \nu(T) T^{-1}$.

The change rate $\nu_{p-LO} = (\partial f_p/\partial t)_{p-LO}$ of distribution function caused by $H_{p-LO}$ involves 2-LO phonons:

$$(\partial f_p/\partial t)_{p-LO} = \sum_{kk'} w(p'k'; pk) \delta(p' + \omega k - \omega k', \epsilon_p)$$

$$n_0(1 - n_0) N_0 (1 + N_0) \frac{\hat{\omega} p' + \chi_k + \hat{\omega} k - \hat{\omega} p}{k_B T}$$

$$+ \sum_{kk'} w(p', k', k; p) \delta(p' + \omega k', \omega k + \epsilon_p)$$

$$n_0(1 - n_0) (1 + N_0) (1 + N_0) \frac{\hat{\omega} p' + \chi_k + \hat{\omega} k - \hat{\omega} p}{k_B T},$$

the first term is caused by scattering of LO-phonon by polaron $p + k' = p' + k'$, where $p$ and $p'$ are wave vectors of polaron before and after scattering, $k$ and $k'$ are wave vectors of the incident and outgoing LO phonons. The 2nd term is caused by the emitting and absorbing 2-LO phonons $p \rightarrow p' + k + k$. Noticing the dispersion of LO phonon is negligible, by a similar procedure deriving Eq. (31), one finds

$$\nu_{p-LO} = \frac{e^{-3/2} (k_B T)^{3/2} k_B}{(2 \pi)^3} \sqrt{\frac{m_p}{3}}$$

(34)

$$\frac{[q^2/2c_0 h (1/\epsilon_\infty - 1/\epsilon_0)]^2}{\sum_{n \neq 0} J_{n_0}^0 J_{n_0}^0 E_n E_0}$$,

FIG. 1. Mobility $\mu$ vs. temperature $T$ of MAPbBr$_3$, experimental data (+) taken from [12]. (a) piezoelectric tetragonal phase, solid line is a fitting based on Eq. (31); (b) non-piezoelectric cubic phase, solid line is a fitting based on Eqs. (32, 34).
where $k_0 = \pi/a_x$ is the wave vector at boundary of Bril- lonzine zone. If $H_{\text{P-LO}}$, Eq. (33) would imply $\mu(T) = q/m_p\nu(T) \propto T^{-3/2}$. But the total changing rate $\nu(T)$ of $f_p$, a sum of those caused by $H_{\text{P-LO}}$ and by $H_{\text{P-LA}}$: $\nu(T) = \nu_{\text{P-LO}} + \nu_{\text{P-LA}}$. Then $\mu(T) \propto T^{-\gamma}$, $\gamma$ is a number between 1 and 3/2. For the intrinsic carriers in non-piezoelectric cubic phase of MAPbBr$_3$, $\gamma = 1.4$ [12] indicates that $H_{\text{P-LO}}$ seems more important than $H_{\text{P-LA}}$. $\gamma = 1.8$ has been observed for intrinsic carriers in orthorhombic phase MAPbI$_3$(Cl) below 150 K [33]. As noticed earlier, piezoelectric effect does not appear in the orthorgonal phase due to the rigid structure. Then $f_p$ is changed by $H_{\text{P-LO}}$ and $H_{\text{P-LA}}$ rather than $H_{\text{P-pie}}$. $\gamma = 1.8$ indicates that $H_{\text{P-LA}}$ is larger than $H_{\text{P-LO}}$.

The piezoelectric polaron-acoustic phonon interaction [18] has weaker temperature dependence than the ordinary polaron-LA phonon interaction [20], which is one of key factors leading to weaker temperature dependence of mobility in tetragonal phase. In Fig. 1(b) we compare the observed mobility [13] with that expected from Eqs. (32,33). Except the parameters used in Sec. V, we use $\gamma_x = 2$, $M_k$ taken as the mass of Pb. $O_{\text{NLO}} \approx 10\text{meV}$ is used due to lack of knowledge of $\varphi_n$ to calculate $f_{\text{P-LO}}$. The agreement is reasonable well.

VIII. INTRINSIC CARRIERS VS. PHOTO-GENERATED CARRIERS

When a halide perovskite is not exposed to light, the properties of material are different to those of material which is shined by light in three aspects. When a material is kept in dark, the concentration of intrinsic carriers is determined by temperature [13,10]. For example, the relatively lower concentration of intrinsic carriers ($10^2\text{cm}^{-3}$) [12] has two consequences: (i) piezoelectric effect exists in non-piezoelectric cubic phase but not in cubic phase. The $T$ and $k$ dependence of the piezoelectric polaron-acoustic interaction [17] are different to those of ordinary polaron-LA phonon interaction [19]; and (ii) the density of states of polarons is higher, the energy conservation delta functions in collision integral is difficult to satisfy. To remove delta function, one has to carry out $k$-integral precisely.

When a sample is illuminated by a beam of light, the majority of carriers are photo-generated, the density $n_e$ of electrons is fixed by the incident flux of photons, not depend on temperature. In normal operation condition, $n_e < 10^18\text{cm}^{-3}$, the polaron gas is non-degenerate. The equilibrium distribution function is

$$f_{0P} \approx n_e4\pi^{3/2}\hbar^3\exp(-\hbar^2p^2/2m_pk_BT)/(2m_pk_BT)^{3/2}.$$ (35)

The relatively higher concentration ($10^{13},\text{cm}^{-3}$) of photo-generated carriers [11,13] has two consequences: (i) even in the tetragonal phase lacking of inversion center, piezoelectric effect is suppressed by the mobile charges. In both tetragonal and cubic phases, the polaron-acoustic phonon interaction is given by Eq. (19); and (ii) the density of states of polaron is higher, it is legitimate to replace the delta function in $H_{\text{P-LA}}$-collision integral with $(\hbar c_k_b)^{-1}$ [10]. When we execute Boltzmann equation analysis, three different aspects between intrinsic carriers and photo-generated carriers naturally produce their different $\mu(T)$ behaviors.

In summary, for the intrinsic carriers in MAPbBr$_3$ we resolved the puzzle that $\mu(T) \propto T^{-1/2}$ in tetragonal phase and $\mu(T) \propto T^{-1.4}$ in cubic phase. The current scheme is consistent with a previous research on the mobility of photo-generated carriers [10], further clarifies the mechanism of charge transport in halide perovskite, and will help improve the charge separation efficiency in perovskite based solar cells.

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