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Effect of Crystal Symmetry on the Spin States of Fe^{3+} and Vibration Modes in Lead-free Double Perovskite $\text{Cs}_2\text{AgBi}(\text{Fe})\text{Br}_6$

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Abstract

We show by electron spin resonance (ESR) and Raman spectroscopies that the crystal phase transition of the lead-free double perovskite $\text{Cs}_2\text{AgBiBr}_6$ has a profound symmetry-breaking effect on the high-spin states of e.g. a transitional metal ion Fe^{3+} and the vibrational modes. It lifts their degeneracy when the crystal undergoes the cubic-tetragonal phase transition, splitting the 6-fold degenerate $S=5/2$ state of Fe^{3+} to three Kramer doublets, and the anharmonic breathing mode T_g of the MBr_6 octahedra ($\text{M} = \text{Ag}, \text{Bi}, \text{Fe}$) into $E_g + A_g$. The magnitudes of both spin and Raman line splitting are shown to directly correlate with the strength of the tetragonal strain field. This work in turn demonstrates the power of the ESR and Raman spectroscopies in probing structural phase transitions and in providing in-depth information on the interplay between the structural, spin and vibrational properties of lead-free double perovskites – a newly-emerging and promising class of materials for low-cost and high-efficiency photovoltaics and optoelectronics.

In recent years solution-processed perovskite semiconductors have attracted great attention as being emerging low-cost competitors of Si-based solar cells¹⁻³. Indeed, perovskites represent the fastest growing materials system in the context of photovoltaics and light-emitting device applications⁴⁻⁶. Power conversion efficiency (PCE) of lead halide perovskite monolithic tandem solar cells has reached 25.9 % in just 10 years^{3,7}, thus fairly competing with the traditional solar cells based on crystalline silicon, cadmium telluride, gallium arsenide and copper indium gallium selenide^{2,3}. A monolithic tandem Si/perovskite solar cells has reached PCE of 25.1%, demonstrating high compatibility to integrate perovskites with the existing mature Si technology⁸.

Major concerns facing large-scale commercial applications of hybrid lead halide perovskite devices are their toxic nature and instabilities^{9,10}, which have motivated intense research efforts in searching for a new class of lead-free perovskites with better stability. By replacing two Pb^{2+} by a pair of non-toxic M^+ and M^{3+} metal ions, the resulting double perovskites with a general formula $\text{A}_2\text{M}^+\text{M}^{3+}\text{X}_6$ (A and M are cations and X is a halide anion, also known as elpasolite) have emerged as an environmentally friendly alternative to lead perovskites for solar cells¹¹⁻¹⁷ as well as for their potential applications as X-ray detectors¹⁸ and light-emitting diodes¹⁹. Among them, inorganic $\text{Cs}_2\text{AgBiBr}_6$ has attracted particular attention because it is highly stable and it shows interesting physical properties like tunable bandgap^{13,20}, long carrier recombination lifetimes¹², long electron-hole diffusion length²¹, excitonic effects and electron-phonon coupling^{22,23}. Its functionalities for optoelectronic devices have just started to be explored. Unfortunately, the solar cell performance of $\text{Cs}_2\text{AgBiBr}_6$, with PCE reaching 2.51%, is far from competing with the lead-based perovskites¹⁶. This calls for a better understanding of the fundamental properties of $\text{Cs}_2\text{AgBiBr}_6$ and related double perovskites including structural, electronic, optical and phonon properties, as well as interactions between them. This is especially important for

Figure 1 **a)** and **b)** crystal structure of $\text{Cs}_2\text{AgBiBr}_6$ in the cubic and tetragonal phases. The insets show the orientation of the BiBr_6 (or FeBr_6 in Fe-doped crystal) octahedral sublattices along the c and a crystallographic axes. **c)** and **d)** The predicted spin splitting patterns of Fe^{3+} (the blue lines) in a magnetic field and the expected ESR transitions at 9.3 GHz (the red vertical lines) in the cubic and tetragonal phases. **e)** and **f)** The Raman modes of the MBr_6 octahedra predicted for the cubic and tetragonal crystal symmetry.

double perovskites as their physical properties are expected to be considerably different from their lead-based counterparts and are more complex due to the interplay between two different sublattices. The gained knowledge on these fundamental properties is essential for designing strategies to tune optoelectronic properties and to identify new compounds of the same class and their low-dimensional counterparts with tailored physical properties for optimal device performance. Indeed, a structural phase transition of $\text{Cs}_2\text{AgBiBr}_6$, from a cubic phase (space group $\text{Fm}\bar{3}\text{m}$ – **figure 1a**) at room temperature to a tetragonal phase (space group I4/m – **figure 1b**) at temperatures lower than the phase transition temperature $T_s \sim 122$ K, has recently been uncovered from studies of X-ray and neutron diffraction²⁴. The local symmetry around $(\text{BiBr}_6)^{-3}$ octahedra reduces from cubic (with the same Bi-Br bond length along the a , b and c crystallographic axes) to axial (with a larger Bi-Br bond length along the c axis than those in the ab plane in addition to a slight twist of the octahedra around the c axis). This structural change was shown to lead to noticeable changes in optical properties monitored in reflectivity, photoluminescence and absorbance measurements, e.g., the

excitonic transition energy near the direct gap shifts proportionally to the strength of tetragonal strain²⁴.

In this work, we examine the effects of crystal phase transition on spin states of transition metal ions such as Fe^{3+} and vibration modes of $\text{Cs}_2\text{AgBiBr}_6$ by employing electron spin resonance (ESR) and Raman spectroscopy. We show that the transition from the cubic to tetragonal crystal phase lifts the degeneracy of the $S=5/2$ spin states of Fe^{3+} into three Kramer doublets ($M_s=\pm\frac{1}{2}, \pm\frac{3}{2}$ and $\pm\frac{5}{2}$) at zero magnetic field with the corresponding zero-field spin splitting scaling with the strength of the tetragonal strain. We also reveal that the crystal symmetry-lowering results in splitting of the T_{2g} vibration mode, and again the extent of the splitting critically depends on the strain field. Our results in turn demonstrate the power of ESR and Raman spectroscopies to sensitively probe the crystal structural change and the strength of the crystal field.

Figure 2 a) Temperature dependent ESR spectra of the Fe-doped $\text{Cs}_2\text{AgBiBr}_6$ crystal powder associated with Fe^{3+} . The red lines are experimental data and the gray lines are the simulated curves from the spin Hamiltonian analysis. **b)** Temperature dependence of the axial (D) and rhombic (E) zero-field splitting parameters deduced from the ESR spectra of Fe^{3+} . The solid line is the fitting curve using the critical exponents function Eq.2.

Typical ESR spectra as a function of measurement temperature from Fe-doped $\text{Cs}_2\text{AgBiBr}_6$, in the form of a large ensemble of small single crystals – equivalent to a powder sample, are shown by the red curves in **figure 2a**. The observed ESR signals are absent in

undoped Cs₂AgBiBr₆ but are found to increase in intensity with increasing Fe doping concentration in Fe-doped Cs₂AgBiBr₆, suggesting their direct association with the Fe doping. At a temperature >125 K, the ESR spectra only exhibit a single line with $g \sim 2.032$. Below 120 K, the single ESR line is replaced by a set of multiple ESR lines with their line spacing increasing with decreasing temperature. The fashion that such multiple ESR lines fan out is characteristic for an ESR spectrum from a high-spin state ($S > 1/2$) undergoing increasing zero-field spin splitting as the strength of a low-symmetry crystal field increases^{25,26}. To obtain in-depth information on the nature and spin configuration of the responsible paramagnetic centre, the ESR spectra are carefully analysed with the aid of the following effective spin Hamiltonian:

$$\hat{H} = g_e \mu_B \mathbf{B} \hat{\mathbf{S}} + D(T) S_z^2 + E(T) (S_x^2 - S_y^2) \quad (1)$$

Here, g_e is the electron Landé g -factor, μ_B the Bohr magneton and $\mathbf{B}$ the magnetic field vector. $\hat{\mathbf{S}}$ is the electron spin operator with components S_x , S_y and S_z . $D(T)$ and $E(T)$ are the temperature dependent axial and rhombic zero-field splitting (ZFS) parameters. From the best fit of the spin Hamiltonian Eq.(1) to the experimental data, the high-spin state observed in ESR at <120K corresponds to the $S=5/2$ state. The only plausible candidate that possesses such spin configuration in Fe-doped Cs₂AgBiBr₆ is Fe³⁺ with the 3d⁵ configuration. This assignment also identifies Fe³⁺ to reside on the M³⁺ site replacing Bi³⁺, which satisfies the conditions for both chemical bonding and charge neutrality.

The spin Hamiltonian analysis also concludes that Fe³⁺ experiences a crystal field of axial symmetry, characterized by the spin-Hamiltonian parameters $D > 0$ and $E = 0$. The non-zero D is responsible for the zero-field spin splitting of the $S=5/2$ states into three Kramers doublets $M_s = \pm \frac{1}{2}, \pm \frac{3}{2}$ and $\pm \frac{5}{2}$, leaving the $M_s = \pm \frac{1}{2}$ spin sublevel at the lowest energy as illustrated in **figure 1d**, and the resulting multiple ESR transitions. From a detailed analysis of

the EPR spectra at various temperatures, the temperature dependent $D(T)$ can be obtained and is plotted in **figure 2b**. $D(T)$ is found to increase with decreasing temperature, replicating the temperature dependence of the spontaneous tetragonal strain determined in the early structural analysis of undoped $\text{Cs}_2\text{AgBi}(\text{Fe})\text{Br}_6$ by X-ray diffraction²⁴. This finding provides a direct proof that the axial crystal field leading to the zero-field splitting of Fe^{3+} originates from the tetragonal strain of the host crystal itself. It can also be clearly seen from **figure 2b** that, when temperature rises towards 120K, $D(T)$ approaches zero and remains so at the higher temperatures. This critical temperature coincides with the crystal phase transition of $T_s \sim 122$ K from the early studies of X-ray and neutron diffraction²⁴. Therefore, we can conclude that the single ESR line observed at $>130\text{K}$ in fact stems from the $S=5/2$ spin state of Fe^{3+} without zero-field splitting ($D=E=0$) such that all ESR transitions occur at the same resonance field as illustrated in **figure 1c**. To obtain a more accurate T_s from the ESR data, we analyse the temperature dependence of $D(T)$ by the following relation^{26,27};

$$D(T)(\text{Fe}^{3+}) \propto (T_s - T)^\alpha. \quad (2)$$

The best fit of Eq.2 to the experimental data yields $T_s = 122$ K, and $\alpha = 1/2$ for a second-order phase transition based on the mean-field theory²⁷. The resulting fitting curve is plotted by the black solid line in **figure 2b**. The obtained T_s value exactly matches that obtained from the X-ray and neutron diffraction²⁴, demonstrating the power of the ESR spectroscopy in accurately sensing the crystal phase transition in addition to its commonly known capability in retrieving microscopic information on the electronic structure and spin configurations.

We note that, though in principle g-factor anisotropy is also expected in the tetragonal phase, an isotropic g factor with $g \sim 2.032$ is deduced within our experimental accuracy throughout the temperature range of 30-300K regardless of the crystal phase transition. The observed absence of g-factor anisotropy is rather common for Fe^{3+} in other materials, as it is

usually within the experimental error²⁵. Using the deduced spin-Hamiltonian parameters, the simulated ESR spectra for powder at different temperatures are also displayed by the grey curves in **figure 2a**. The excellent agreement between these simulated ESR spectra and the experimental data further justifies our conclusion on the evolution of the Fe³⁺ spin state accompanying the crystal phase transition of Cs₂AgBiBr₆ from the cubic to tetragonal symmetry.

Figure 3 **a)** Raman spectra at 30 K, 60 K, 140 K and 300 K under the 532-nm laser pumping. Raman Intensity at 300 K is enlarged by a factor of two for a clear comparison. The Raman signal at 30 K are fitted with Lorentzian curves in grey. **b)** Schematic pictures of the dominant Raman modes $A_g(1)$, $E_g(2)$ and $T_g(3)$. **c)** Contour plot of Raman spectra v.s. temperature of $T_g(3)$, $E_g(2)$ and $A_g(1)$. **d)** and **e)** Linewidths and peak positions of these Raman modes as a function of temperature. The dash lines mask the phase transition temperature.

Room-temperature carrier-phonon interactions and the vibrational modes associated with the MBr₆ octahedra in Cs₂AgBiBr₆ were reported early and a strong Fröhlich interaction was suggested^{22,23,28}. The dominant Raman modes of the cubic phase have been identified at 75, 135 and 175 cm⁻¹ that belong to T_g (enharmonic breathing), E_g and A_g (both stretching) modes^{23,28} of either (BiBr₆)³⁻ octahedra²⁸ or (AgBr₆)⁵⁻ octahedra²³, as schematically illustrated in **figure 3b**. The subscript g refers to a Raman active mode. Up to now, nothing is known about the vibrational modes of the tetragonal Cs₂AgBiBr₆ after the crystal phase transition.

In principle, a crystal-symmetry reduction from $Fm\bar{3}m$ to $I4/m$ is also expected to lift the degeneracy of some vibrational modes associated with the octahedral sublattices. For example, the three-fold degenerate Raman active mode of $T_g(3)$ is predicted to split into $E_g(2) + A_g(1)$ based on group theory (see **figure 1e** and **1f**). Here, the number in each parenthesis refers to the degeneracy of the modes.

Apart from the three Raman modes of the MBr_6 octahedra, the crystal symmetries also allow Raman scattering of low-frequency lattice modes, as was observed in elpasolites^{29–31}. The absence of such Raman modes in our study could possibly be due to their low frequencies ($< 50\text{ cm}^{-1}$) that are beyond the range of our instrumental coverage.

To evaluate the influence of the crystal phase transition, we studied the dominant Raman modes over a wide temperature range of 30-300 K. **Figure 3a** shows representative Raman spectra measured at 30 K, 60 K, 140 K and 300 K, taken as an example from the Fe-doped $Cs_2AgBiBr_6$ crystal along a $\langle 111 \rangle$ crystallographic axis. At room temperature three Raman modes are observed that agree with the previously identified modes of $T_g(3) \sim 72\text{ cm}^{-1}$, $E_g(2) \sim 133.8\text{ cm}^{-1}$ and $A_g(1) \sim 176.2\text{ cm}^{-1}$ from the undoped $Cs_2AgBiBr_6$, showing that they originate from the vibrational modes of the pristine crystal that are unaffected by the Fe doping.

An overview of the temperature dependence of these three Raman modes is given in **figure 3c**, whereas their linewidths and peak positions deduced from the fitting with Lorentzian lines are shown in **figure 3d and 3e**. For all modes, the linewidths monotonically decrease from $\sim 10\text{ cm}^{-1}$ towards $\sim 3\text{ cm}^{-1}$, with an apparent change of the slope near T_s for the $T_g(3)$ mode. We tentatively attribute this linewidth narrowing of the Raman modes to a reduced contribution of thermal bath. In contrast, the peak positions of all three Raman modes exhibit striking variations near T_s . For the $T_g(3)$ mode, it splits into two components at $T < T_s$, i.e. $E_g(2) +$

$A_g(1)$ as predicted by group theory. The magnitude of the splitting is proportional to the strength of the tetragonal strain. Furthermore, the peak position of $T_g(3)$ in the cubic phase displays an anomalous behaviour of mode softening, namely, its frequency reduces from $\sim 72.5 \text{ cm}^{-1}$ to $\sim 71.4 \text{ cm}^{-1}$ upon cooling down towards T_s . This frequency reduction is in fact opposite to what is usually expected from hardening (i.e. a frequency increase) of a Raman mode accompanying by shrinking of lattice constants upon cooling, as seen for $E_g(2) \sim 133.8 \text{ cm}^{-1}$ and $A_g(1) \sim 176.2 \text{ cm}^{-1}$ to be discussed below. The observed frequency reduction of $T_g(3)$ when temperature approaches T_s from both cubic and tetragonal phases, on the other hand, resembles a ‘soft-phonon’ lattice mode³². This finding might indicate a link between the $T_g(3)$ mode and the lattice vibrations that are important to the phase transition.

In contrast to $T_g(3)$, both $E_g(2) \sim 133.8 \text{ cm}^{-1}$ and $A_g(1) \sim 176.2 \text{ cm}^{-1}$ exhibit the character of hard Raman modes. In the cubic phase, their frequencies increase with decreasing temperature from 133.8 to 138.1 cm^{-1} and from 176.2 to 179.1 cm^{-1} , respectively (see **figure 3e**), as expected from symmetric shrinking of lattice parameters that increases total energy of the symmetric octahedral vibrational modes. This trend discontinues at T_s . For $A_g(1) \sim 176.2 \text{ cm}^{-1}$ mode, the mode frequency becomes lower as temperature further decreases. This could be understood by considering an asymmetric modification of the $M\text{Br}_6$ ($M=\text{Ag}$ or Bi) bond length below T_s . For the AgBr_6 octahedra, the bond length in the ab plane ($\text{Ag}-\text{Br}_{a,b}$) gradually changes from 2.8 to $2.785 \text{ \AA}$ ($\sim 0.53\%$) as temperature reduces from 130 to 30 K , whilst the bond length of $\text{Ag}-\text{Br}_c$ increases from 2.8 to $2.838 \text{ \AA}$ (1.35%). This translates to an increase of the effective octahedral volume and, therefore, a decrease of the $A_g(1)$ mode frequency below T_s . For the $E_g(2) \sim 133.8 \text{ cm}^{-1}$ mode, on the other hand, it keeps hardening below T_s but at a lower rate. This difference in the temperature dependence between $A_g(1)$ and $E_g(2)$ below T_s may stem from the fact that the $E_g(2)$ mode transforms into $A_g(1) + B_g(1)$ modes and the frequency

difference between these two modes cannot be simply predicted under the effective volume consideration. Even at 30K, the splitting of $E_g(2)$ remains unresolved, possibly due to a large Raman linewidth.

There is an appearance of a weak satellite Raman mode at 172 cm^{-1} near the shoulder of the main 178.7 cm^{-1} $A_g(1)$ at 30 K in both Fe-doped and undoped samples. This mode resembles that seen in the low-temperature Raman spectra from Rb_2KScF_6 crystals in the monoclinic phase³⁰, where such a transition belongs to a formally inactive $X(0, 0, \pi/a)$ Raman mode in the cubic phase that becomes allowed in the monoclinic phase with a double primitive cell volume. From the previous XRD analysis of undoped $\text{Cs}_2\text{AgBiBr}_6$ ²⁴ and also our own XRD analysis of $\text{Cs}_2\text{AgBi(Fe)Br}_6$ at 30 K, the crystal symmetry deduced from the Rietveld refinement remains to be the space group $I4/m$ of tetragonal symmetry. At present, the exact origin of the Raman mode at 172 cm^{-1} remains unknown, which calls for further careful structural studies of $\text{Cs}_2\text{AgBiBr}_6$ at and below 30 K.

In summary, we have shown from the ESR and Raman spectroscopies that the crystal phase transition of the lead-free double perovskite $\text{Cs}_2\text{AgBiBr}_6$ has a profound effect on the high-spin states of e.g. a transitional metal ion Fe^{3+} (residing on the Bi site) and the vibrational modes. The structural phase transition predominantly manifests itself as a source of symmetry-breaking that lifts the degeneracy of the spin states and Raman modes when the crystal undergoes a transition from the cubic to tetragonal phase. This splits the 6-fold degenerate $S=5/2$ state of Fe^{3+} to three Kramer doublets $M_s = \pm\frac{1}{2}, \pm\frac{3}{2}$ and $\pm\frac{5}{2}$ at zero magnetic field, thereby transforming the corresponding ESR spectra from a single line to a set of multiple lines. The size of the zero-field spin splitting is shown to directly correlate with the strength of the tetragonal strain field. A similar symmetry-reduction effect is found for the enharmonic breathing mode $T_g(3)$ of the MBr_6 octahedra, which splits into $E_g(2) + A_g(1)$ below the phase

transition temperature T_s with the extent of the splitting scaling with the tetragonal strain field. Anomalous softening of the $T_g(3)$ mode near T_s is observed, unlike the stretching modes E_g and A_g of the MBr_6 octahedra that exhibit expected hardening when the temperature decreases. The observed high sensitivity of the ESR and Raman spectroscopies to a small degree of lattice distortion in turn demonstrates the power of these techniques in probing structural phase transitions and in providing in-depth information on the interplay between the structural and spin properties of lead-free double perovskites – a newly-emerging and promising class of materials relevant to low-cost and high-efficiency photovoltaic and optoelectronic applications.

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Methods

Sample preparation - Solid CsBr (213 mg, 1.00 mmol), BiBr₃ (135 mg, 0.3 mmol) and FeBr₃ (59.1 mg, 0.2 mmol) were dissolved in 4 mL of 47% HBr. Solid AgBr (94 mg, 0.5 mmol) was then added. The mixed solution was transferred to Teflon-lined digestion bomb and placed in the oven where it was heated at 120 °C for 24 h. The crystal of Fe-doped Cs₂AgBiBr₆ was then formed after the mixture was slowly cooled down to room temperature.

ESR – ESR was performed with a Bruker Eleksys E500 spectrometer operating at about 9.3 GHz. ESR spectra were recorded in dark. Crystal powder was prepared via gliding several Fe-doped or undoped Cs₂AgBiBr₆ single crystals into a large number of small pieces. The powder was sealed in an evacuated quartz tube and placed in a He-flow cryostat.

Raman spectroscopy – Raman measurements were carried out using a confocal Horiba Jobin-Yvon HR800 system. A 1800 l/mm single-grating monochromator in the conjunction with a Si charge-coupling-device (CDD) array (1024 by 256-pixel counts) were used. This translated to a spectral resolution better than 1 cm⁻¹, with pixel counting of 4 pixels/cm⁻¹. A solid-state diode laser with a wavelength of 532 nm was used as a pumping source, with power below 1 mW μm⁻² to avoid sample heating. 532 nm edge filters (Semrock LE03-532RE-25 with edge steepness of 37.5 cm⁻¹) were used to filter out the laser line. The edge filter and the single-grating

monochromator limited the detection of Raman modes with wave numbers below 50 cm^{-1} . The induced Raman scattering signals were collected via a $50\times$ objective with $\text{NA}=0.5$ in a back-scattering geometry. The light beam was directed parallel to a $\langle 111 \rangle$ crystallographic direction of an undoped or Fe-doped $\text{Cs}_2\text{AgBiBr}_6$ single crystal. The samples were mounted in a He flow cryostat. Temperature stability was better than 0.5 K .

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TOC/abstract graphics