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**The Rotationally Free and Rigid Sublattices of the Single Crystal Perovskite
CH₃NH₃PbBr₃ (001): The Case of the Lattice Polar Liquid**

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Abstract

The dynamic motion, within the lattice of single crystal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (001) hybrid halide perovskite, was investigated using powder and single crystal x-ray diffraction, and x-ray photoemission spectroscopy. Single crystal x-ray diffraction studies indicate the methylammonium cation adopts multiple orientations within the crystal, at room temperature, evidence of a disordered methylammonium sublattice within a rigid and ordered PbBr_3 matrix lattice. From the Br $3d_{5/2}$ core level photoemission temperature dependence, an effective Debye temperature of 160 ± 22 K can be estimated, while the Pb $4f_{7/2}$ core-level Debye-Waller factor plots suggest an effective Debye temperature of 202 ± 131 K, indicative of a very rigid lattice along the (001) direction. The combination of x-ray diffraction with temperature dependent x-ray photoemission spectroscopy for bromine and lead core level peaks support the characterization of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as a lattice polar liquid crystal, as $\text{CH}_3\text{NH}_3\text{PbBr}_3$ does not meet the criteria required for a ferroelectric material.

Introduction

The organic-inorganic halide based perovskites (OIHPs) have captured the attention of the scientific community for the past decade, with halide based perovskites having a rich history dating back nearly 125 years.^{1,2} The advent of OIHPs occurred in 1978 with the first synthesis of methylammonium lead iodide, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), by Dieter Weber.^{3,4} Between 1980 and the mid-2000s the crystal structures and dynamics of the OIHPs had been extensively studied using x-ray diffraction (XRD), neutron powder diffraction, nuclear magnetic resonance (NMR), and millimeter-wave interferometry.^{5–12} In 2009, interest in these materials dramatically increased after Kojima *et al.*¹³ first used hybrid perovskite MAPbI_3 in a solar cell structure, producing a device efficiency of 3.8%. Due to the enormous attention from the scientific community, OIHPs have seen an impressive boost in photovoltaic device efficiency to over 22% by 2016.¹⁴ Research has shown that the hybrid perovskites possess many interesting material properties such as long carrier diffusion lengths, long effective carrier lifetime, large absorption coefficients, and ambipolar charge transport.^{13,15–21} Additionally, hybrid perovskites have shown up in many applications other than photovoltaics ranging from photodetection,^{22,23} high energy radiation detection,²⁴ lasers,^{25–27} light emitting diodes,^{28–32} spintronics,³³ and thermoelectrics.^{34,35} While the amount of research related to the OIHPs is staggering and the improvements in device performance are quite impressive, the underlying physical phenomena are not well understood, and with some explanations embroiled in controversy.

At the center of one controversy is the observed hysteresis in current-voltage (I-V) measurements performed on a wide range of the hybrid halide perovskites. Many researchers have posited several explanations regarding the nature of the observed hysteresis: ferroelectricity,^{36–58} ion migration,^{59–67} charge trapping,^{68–70} capacitive effects,^{61,71–74} and photo

induced effects,⁷⁵ leading to the impression that there is no uniform view with regards to the physics responsible for the hysteretic effects observed in I-V measurements. While the explanation of ferroelectricity in the hybrid lead halide perovskites is appealing; as this hypothesis suggests a dipole-induced intrinsic electric field which would go a long way towards explaining the charge collection efficiencies, rather than attributing more responsibility to the band structure and band alignment across the interfaces of a device. Upon closer inspection there is little to support the contention that the hybrid lead halide perovskites are ferroelectric.

Despite the debate about the hysteretic effects observed in the organic-inorganic halide perovskites, there are many studies that have elicited interesting physics, specifically for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3). For example, as mentioned above, investigations of surface charging are numerous and perplexing. Complicating the investigation of surface charge accumulation are the complexities that occur at the surface. An example of one of the many issues that affect the surface was the MABr surface termination of single crystalline $\text{MAPbBr}_3(001)$.⁷⁶ Furthermore, the $\text{MAPbBr}_3(001)$ tends to have segregation of metallic lead to the surface.^{77–79}

A few experimental band structure measurements have been performed such as the study by Komesu *et al.*⁷⁶ whereby angle resolved photoemission spectroscopy was employed in order to observe that the top of valence band has a bulk band MABr contribution. An experiment on methylammonium lead iodide single crystals by Lee *et al.* measured the dispersion in $k_{\perp}$ at the surface Brillouin zone edge but with a wave vector along the surface normal, i.e. a photon energy dependent study, using angle resolved photoemission.⁸⁰ From the Lee *et al.* study the bulk band character of the top of the valence band was established. This conclusion was confirmed by resonant photoemission spectroscopy, in combination with theory, to show that indeed the valence band is dominated by Pb-Br hybridized bulk bands refuting the notion that the top of the

valence band is dominated by surface bands.⁸¹ The light hole effective mass, evident in the experimental band structure of single crystalline MAPbBr₃,⁷⁶ is consistent with higher carrier mobilities and the extremely long carrier diffusion lengths on the order of 10 μm ¹⁷ suggesting a potential for efficient devices and reasonably high charge extraction. There are many other studies featuring interesting physics associated with MAPbBr₃ which we will not further discuss here.

Here, powder x-ray diffraction, single crystal x-ray diffraction, and photoemission spectroscopy techniques were used to investigate the lattice stiffness (and indirectly the dynamic motion) of single crystalline MAPbBr₃(001).

Experimental Methods

Single crystals of MAPbBr₃, with synthesis described elsewhere,⁸² of approximate dimensions 5 x 5 x 1 mm³ were examined using x-ray photoemission spectroscopy (XPS). MAPbBr₃ samples were attached to molybdenum sample plates using silver epoxy (EPO-TEK H21D) and then fractured in ultra-high vacuum before initial measurement, via abrupt contact with a linear translator. Fracturing in vacuum exposes a fresh surface of MAPbBr₃ reducing the effects of surface contamination due to environmental factors such as air, moisture, and light, which have been shown to influence the organic-inorganic halide perovskites.^{83–88} Core level XPS was performed using a SPECS X-ray Al anode ($h\nu = 1486.6 \text{ eV}$) source and a Phi hemispherical electron analyzer (PHI Model 10-360) with an angular acceptance of $\pm 10^\circ$ or more. All XPS was performed in an ultra-high vacuum chamber with a base pressure better than 1×10^{-10} mbar. Samples were cooled via a cold finger through a temperature range of 225-240 K using liquid nitrogen.

Powder x-ray diffraction (XRD) measurements were performed with a Rigaku Smart Lab diffractometer, equipped with a Cu K α source, $\lambda = 1.54 \text{ \AA}$. All XRD was performed at room temperature in air. The scanning parameters were as follows: scan range of 10-90°, step size of 0.1 degree, and dwell time of 2 degrees/min.

Single crystal XRD was performed from 100-300 K with a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector. The MAPbBr₃ crystal, orange in color, (approximate dimensions $0.24 \times 0.24 \times 0.23 \text{ mm}^3$) was placed onto the tip of a 0.05 mm diameter glass capillary and mounted on the diffractometer.

The single crystal XRD data collection was carried out using Mo K α radiation (graphite monochromator), $\lambda = 0.71073 \text{ \AA}$, with a frame time of 5 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.50 $\text{\AA}$ with a redundancy of 4 were collected. Eight major sections of frames were collected with 0.50° ω and ϕ scans. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.⁸⁹ The integration of the data using a cubic unit cell yielded a total of 7154 reflections to a maximum θ angle of 43.03° (0.52 $\text{\AA}$ resolution), of which 198 were independent (average redundancy 36.131, completeness = 100.0%, $R_{\text{int}} = 6.88\%$, $R_{\text{sig}} = 1.93\%$) and 192 (96.97%) were greater than $2\sigma(F^2)$.

The space group for the MAPbBr₃ crystal was determined based on intensity statistics and systematic absences. The structure was solved and refined using the SHELX suite of programs.⁹⁰ An intrinsic-methods solution was calculated, which provided most non-hydrogen atoms from the E-map.⁹⁰ Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. Pb and Br were refined with anisotropic

displacement parameters; C and N were refined with common isotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final anisotropic full-matrix least-squares refinement on F^2 with 13 variables converged at $R1 = 2.24\%$, for the observed data and $wR2 = 4.37\%$ for all data. The goodness-of-fit was 1.313. The largest peak in the final difference electron density synthesis was $0.561 \text{ e}/\text{\AA}^3$ and the largest hole was $-1.214 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.241 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $3.844 \text{ g}/\text{cm}^3$ and $F(000)$, 206 e^- . The remaining electron density is minuscule and located near CH_3NH_3^+ . C and N are disordered with one another located near a special position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with site symmetry $m-3m$) generating 48 possible and symmetry equivalent orientations of the molecule. A C-N distance constraint, based on literature values for methyl ammonium moieties, was applied as the electron density at the sites of the atoms is low and diffuse because of the site symmetry.

Results and Discussion

As noted above, many studies on the organic-inorganic halide perovskites have suggested that the observed hysteretic effects observed in I-V measurements are due to intrinsic ferroelectric properties of the materials.³⁶⁻⁵⁸ A ferroelectric phase, in the organic-inorganic halide perovskites, has the benefit of plausibility as the methylammonium ion has a natural dipole. Many other perovskites such as BaTiO_3 are known to exhibit ferroelectricity,⁹¹ so it is not unreasonable to suspect that the OIHPs possess a ferroelectric phase. Then the question becomes, “Is this in fact a correct characterization?” It is instructive to first define ferroelectricity and list the requirements that must be satisfied for a material to be labeled as a true ferroelectric. Ferroelectricity, like ferromagnetism, refers to the alignment of an electronic moment i.e. a dipole in a material which produces a net polarization or moment. A rigorous definition of

ferroelectricity includes the following requirements: 1) Spontaneous polarization must be present in the absence of an applied electric field, 2) Spontaneous and induced polarizations must be switchable, 3) A critical or coercive voltage exists; below this voltage any induced polarization vanishes after removing the applied field and above this voltage the polarization eventually saturates, 4) A remnant polarization must be maintained after removal of an applied external electric field such that the polarization remains for an extended period of time: hours, days, months, etc., 5) A critical temperature exists, below which the material exhibits ferroelectric properties i.e. a Curie temperature and above which the material exhibits no ferroelectric nature. There are rare cases in which the ferroelectric material has a Curie temperature which is above the melting temperature of the material, such as in the case of polyvinylidene fluoride (PVDF).⁹² The final criteria is, 6) the crystal symmetry must be non-centrosymmetric i.e. there should be no inversion symmetry.^{93–97} These 6 criteria will be referred to as the ferroelectricity criteria, FEC, from here forward. To the best of our knowledge there is no evidence from literature suggesting that all of these requirements have been met by MAPbBr₃.

The prototypical perovskite crystal configuration can be described as a composition of ABX₃. In the organic-inorganic halide perovskites A is usually an organic cation, such as methyammonium, CH₃NH₃⁺, or formamidinium, CH(NH₂)₂⁺, with large ionic radii.⁹⁸ The B site ion is usually a smaller metal, such as Pb²⁺ or Sn²⁺, and the X site anion is usually a halide atom such as I, Br, or Cl.^{88,99} Generally, stable hybrid halide perovskites are governed by the choice of atoms/molecules, which are usually determined by the Goldschmidt tolerance factor expressed in Equation (1),¹⁰⁰

$$T_F = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)} \quad (1)$$

where R_A , R_B , and R_X are the effective ionic radii of the A site cation, B site ion, and X site halide, respectively. The ideal situation is when T_F is equal to one, but in the case of organic-inorganic halide perovskites the suitable tolerance factor can range from 0.9 – 1.0 and still maintain the crystal stability.^{98,101–103} The A site cation is coordinated to 12 X site anions, while the B site metal is bonded to 6 of the X site anions. In the case of MAPbBr₃, the MA⁺ ion resides in a cage comprised of eight corner sharing PbBr₆ octahedra. It has been shown that MAPbBr₃ exhibits a cubic to tetragonal I phase transition at roughly 234 K, where the cubic phase is Pm-3m symmetry and the tetragonal I phase is I4/mcm symmetry.^{5,10,104,105} A second phase transition occurs at approximately 155 K when MAPbBr₃ changes from tetragonal I to tetragonal II, where tetragonal II has P4/mmm symmetry.^{5,10,104,105} Then there is a third phase transition at about 147 K from tetragonal II to orthorhombic, where the orthorhombic phase is Pnma symmetry.^{5,7,9} The MAPbBr₃ samples examined in this study are in the cubic phase with a single preferred orientation along the (001) plane as indicated by the powder XRD data, in Figure 1 a, in agreement with the literature.^{106,107} In order to assign a space group and delve deeper into the crystal structure, single crystal XRD was performed, showing that MAPbBr₃ crystallizes at room temperature in the centrosymmetric, cubic space group Pm-3m with the unit cell parameter $a = 5.91460 \text{ \AA}$ and a cell volume of $206.907 \text{ \AA}^3$, also in agreement with literature.^{5,8,107} A detailed set of tables of atomic coordinates, displacements, bond lengths, and bond angles determined by single crystal XRD can be found in the Supporting Information. Since the structure exhibits centro-symmetric symmetry, as such, these perovskites violate typical ferroelectricity criteria, FEC 6, by featuring inversion symmetry. The single crystal XRD data also indicate that methyl ammonium is disordered over 48 orientations as it is located near a special position with site symmetry m-3m, shown in Figure 1 b and c, while the PbBr₃ matrix remains well-defined. Thus,

the methylammonium sublattice is rigidly fixed, but rotationally free while the PbBr_3 sublattice is very rigid. This makes sense as the MA^+ ion has C_{3V} symmetry¹⁰⁸, but it resides in a cubic symmetry PbBr_6 octahedral cage, specifically with O_h symmetry, which suggests the MA^+ ion must be disordered to satisfy the higher symmetry of the perovskite cage. We may conclude from the disorder of the methylammonium ion in addition to the Pm-3m symmetry of the single crystal, at room temperature, the MAPbBr_3 system is not ferroelectric. If the different phases of MAPbBr_3 are closely inspected it is noticeable that all phases, from the room temperature cubic, measured in this study, to tetragonal and orthorhombic, have centrosymmetric symmetry violating FEC 6, which suggests MAPbBr_3 may not be ferroelectric at any temperature.

Figure 1a) Powder XRD spectra indicating high quality single crystal MAPbBr_3 with preferential orientation along (001) plane, inset: Single crystal XRD spectra confirming (001) preferential orientation, b) ball and stick packing model of MAPbBr_3 ; all disorder omitted for clarity, bromine (red), lead (black), and MA (blue, grey, & white) c) packing model based on single crystal XRD, showing disorder of CH_3NH_3^+ ; bromine disorder omitted for clarity; bromine and lead atoms shown as ellipsoids at 50% probability level.

It is well known that the motions of atoms in the bulk and at the surface can be described by the Debye temperature, θ_D . Indeed, many studies using reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), atomic beam scattering, ion beam scattering, XRD, and XPS have been used to extract an effective Debye temperature from several different materials.¹⁰⁹⁻¹²⁰ The true Debye temperature has dominating contributions from in-plane and out-of-plane harmonic and anharmonic motions. However, the effective Debye temperature is associated with atomic motions normal to the crystal surface and parallel to a scattering vector, Δk , and typically has no significant contributions from anharmonic or in-plane motions.¹⁰⁹⁻¹¹⁹ In XPS the intensity of the ejected electrons decays exponentially with increasing temperature due to an increase in thermal vibrations. As such, the intensity of the photoemission peak can be represented by the following equation:^{110-116,119,120}

$$I = I_0 e^{-W(T)} \quad (2)$$

where $W(T)$ is known as the Debye-Waller factor, T is the temperature of the sample in Kelvin.

Under the assumptions of the isotropic Debye model the Debye-Waller factor is governed by the root mean square atomic displacement, $\langle u_o^2 \rangle$, due to thermal vibrations and by a momentum transfer, Δk , during elastic scattering processes. $W(T)$ can be approximated by,^{114,120}

$$W(T) \cong \frac{1}{2} \Delta k^2 \langle u_o^2 \rangle T \quad (3)$$

The root mean square atomic displacement can be defined under the guidance of the Debye model by the following expression,^{109,118,120}

$$\langle u_o^2 \rangle = \frac{3\hbar^2}{mk_B\theta_D^2} \quad (4)$$

where m is the mass of the scattering center and is determined by the atom of origin in XPS, and k_B is the Boltzmann constant. Finally, by substituting Equation (4) into Equation (3) the Debye-Waller factor¹⁰⁹⁻¹¹⁹ can be explicitly written as,

$$W(T) = \frac{3\hbar^2\Delta k^2T}{2mk_B\theta_D^2} \quad (5)$$

where $\hbar\Delta k$ is the electron momentum transfer, which is approximated by using the kinetic energy of the photoelectron.

The temperature dependent XPS intensity for the Pb 4f core level and Br 3d core level peaks are

Figure 2a) XPS spectra of Pb 4f core level at temperatures from 225 K to 240 K b) XPS spectra of Br 3d core level at temperatures from 225 K to 240 K c) Debye-Waller factor ($=\text{Log}(I/I_0)$) vs temperature for Pb 4f XPS core level, linear fitting indicates an effective Debye temperature of $202 \pm 13\text{K}$, green point is the result of a low photoemission intensity that occurs at a phase transition(see text) d) Debye-Waller factor vs temperature for Br 3d XPS core level, linear fitting indicates an effective Debye temperature of $160 \pm 22\text{K}$

shown in Figure 2 a and b, respectively. These peaks were measured as a function of temperature near the phase transition from the cubic to the tetragonal I phase. The Pb 4f_{7/2} and 4f_{5/2} peaks are centered at 139.84 eV and 144.71 eV, respectively, while the Br 3d_{5/2} and 3d_{3/2} peaks are centered at 69.48 eV and 70.44 eV, respectively. It is important to mention that no metallic Pb peaks were observed in the XPS spectra, which are typically associated with the degradation of the sample.^{76–79,121,122} Thus the sample has not undergone photo-degradation during the measurements. The natural logarithm of the normalized photoemission intensity as a function of temperature is plotted in Figure 2 c and d, for both the Pb 4f_{7/2} and Br 3d_{5/2} core level peaks, respectively. By fitting the data in Figure 2 c and d with a linear function, the slope corresponding to the Debye-Waller factor can be extracted and used to determine the effective Debye temperature. Notice, from Figure 2 c, the Pb 4f_{7/2} peak intensity shows very small temperature dependence, which is indicative of a Pb lattice that is very rigid, almost refractory. The extracted Debye temperature of Pb is determined to be 202 ± 131 K. The small dip in photoemission intensity at 230 K, represented by a green data point in Figure 2 b, is due to the Pb atom motion, the result of structural instabilities at cubic to tetragonal I phase transition as confirmed by temperature dependent single crystal x-ray diffraction, see Supporting Information, and is not considered in the fitting for extracting the Debye temperature. However, there is a clear temperature dependence of the Br 3d_{5/2} intensity and the extracted effective Debye temperature of Br is determined to be 160 ± 22 K. Considering that the generally accepted Debye temperature of Pb is 90.3 K¹²³ and the Debye temperature of Br is 62.4 K,¹²⁴ the data suggests that the PbBr₃ sublattice is very rigid, in agreement with the single crystal XRD. Of course, the XPS data does not indicate the Debye temperature or motion of the methylammonium. However, due to the disorder of the methylammonium based on single crystal XRD it is reasonable to say

that methylammonium forms a soft sublattice. In fact, this material falls more in line with what is known as a lattice polar liquid which will be discussed below and this notion has been suggested before although not deeply discussed.^{26,43,125}

In 1936 Lars Onsager described a molecular dipole in a cavity field based on classical dynamics, which was developed to better understand the interaction of a molecular dipole moment with the dielectric constant of its environment.¹²⁶ Subsequently in 1937 J.H. Van Vleck derived from Onsager's cavity field paper the criteria for a polar liquid.¹²⁷ Van Vleck established that a polar liquid must meet the following criteria: 1) There must exist an absence of spontaneous polarization over a wide range of temperature, 2) there must exist a "congealing" of dipoles below some critical temperature, where "congealing" refers to a hindered rotation of the dipoles, 3) the dielectric constant must exhibit a discontinuity in a temperature profile, 4) the dipoles must be freely rotating above the critical temperature, and 5) at high applied electric fields the dielectric constant must cease to be independent of the field strength. The 5 criteria above will be referred to as the polar liquid criterion, PLC, from here forward. If one looks at the wide body of literature centered on MAPbBr₃ it is clear the PLCs are satisfied. PLC 1 was satisfied with the observation by Xiao *et al.* that no spontaneous polarization occurred over a wide temperature range in MAPbBr₃.⁶² The "congealing" of the dipoles (PLC 2) has been measured using single crystal XRD, NMR, and adiabatic calorimetry, all of which showed MAPbBr₃ in the low temperature orthorhombic phase had restricted rotation of MA dipoles. Furthermore, at the high temperature tetragonal and cubic phases the MA dipoles were disordered and freely rotating, as shown in the current study and thus also satisfying PLC 4.⁵⁻⁹ The dielectric constant of MAPbBr₃ was shown to exhibit a stark discontinuity when transitioning from the tetragonal phase to the orthorhombic phase thus satisfying PLC 3.^{10,105,128}

Finally, regarding PLC 5 the dielectric constant at high electric field was shown to increase as a function of voltage by Anusca *et al.* based on the slope of the polarization-voltage curve.¹²⁹ We therefore conclude that MAPbBr₃ is a lattice polar liquid rather than a ferroelectric material.

Conclusion

This study has confirmed the coexistence of a soft-disordered methylammonium sublattice and a rigid-ordered PbBr₃ sublattice in MAPbBr₃. Furthermore, as indicated elsewhere MAPbBr₃ is in fact a lattice polar liquid.^{26,43,125} Methylammonium lead bromide cannot be a ferroelectric or an electret at room temperature due to gross failures to meet the essential requirements. This means that the electron-hole separation, which leads to large current generation in a photovoltaic, is a result of band structure, not a dipole-induced intrinsic field as has been previously suggested. Large charge collection efficiencies thus do not always require a large intrinsic electric field.

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Supporting Information

Supporting Information Available: Detailed list of temperature dependent single crystal x-ray diffraction data: crystal data, atomic coordinates, and structure refinement. This material is available free of charge via the Internet at <https://pubs.acs.org/>

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TOC Graphic

Figure 1a) Powder XRD spectra indicating high quality single crystal MAPbBr3 with preferential orientation along (001) plane, inset: Single crystal XRD spectra confirming (001) preferential orientation, b) ball and stick packing model of MAPbBr3; all disorder omitted for clarity, bromine (red), lead (black), and MA (blue, grey, & white) c) packing model based on single crystal XRD, showing disorder of CH3NH3+; bromine disorder omitted for clarity; bromine and lead atoms shown as ellipsoids at 50% probability level.

64x164mm (300 x 300 DPI)

Figure 2a) XPS spectra of Pb 4f core level at temperatures from 225 K to 240 K b) XPS spectra of Br 3d core level at temperatures from 225 K to 240 K c) Debye-Waller factor ($=\text{Log}(I/I_0)$) vs temperature for Pb 4f XPS core level, linear fitting indicates an effective Debye temperature of 202 ± 131 K, green point is the result of a low photoemission intensity that occurs at a phase transition (see text) d) Debye-Waller factor vs temperature for Br 3d XPS core level, linear fitting indicates an effective Debye temperature of 160 ± 22 K

93x90mm (300 x 300 DPI)