Analytic dependence of the Madelung constant on lattice parameters for 2D and 3D metal diiodides (MI₂) with CdI₂ (2H polytype) layered structure

V S Harutyunyan

Department of Solid State Physics, Yerevan State University, 0025 Yerevan, Armenia
E-mail: vharut@ysu.am

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Abstract

In this theoretical study, the Madelung constant ($A_M$) both for a 2D layer and parent 3D bulk crystal of metal diiodides $\text{M}_2\text{I}_2$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{Cd}, \text{Pb}$) with CdI₂ (2H polytype) structure is calculated on the basis of the lattice summation method proposed in author’s earlier work. This method enabled, both for a 2D layer and 3D bulk crystal of these compounds, to obtain an analytic dependence of the Madelung constant, $A_M(a, c, u)$, on the main crystallographic parameters $a$, $c$, and $u$. The dependence $A_M(a, c, u)$ reproduces with a high accuracy the value of the constant $A_M$ not only for metal diiodides $\text{M}_2\text{I}_2$ with CdI₂ (2H polytype) structure, but also for metal dihalides (MX₂) and metal dihydroxides [M(OH)₂] with the same structure. With the use of the high-pressure experimental results available in literature particularly for FeI₂, it is demonstrated that the analytic dependence $A_M(a, c, u)$ is also valid for direct and precise analysis of the pressure-dependent variation of the Madelung constant.

1. Introduction

Layered materials comprise a broad variety of crystalline inorganic compounds with different types of crystallographic structure [1, 2]. In terms of atomic bonding, in such a type materials the strength of atomic bonding in individual layers (intralayer cohesive energy) substantially prevails over that of the atomic bonding between layers (interlayer cohesive energy). Typical examples of layered materials are graphite [3, 4], metal dichalcogenides (e.g., MoS₂, WS₂, MoSe₂, MoTe₂, and Bi₂S₃) [5–9], metal dihalides (e.g., CdI₂, FeI₂, CoBr₂, and MnCl₂) [2], metal dihydroxides (e.g., Co(OH)₂, Mn(OH)₂, and Ca(OH)₂) [2, 10], and some materials with other chemical compositions [1, 2, 6]. Physicochemical properties of individual layers and 2D nanosheets of layered materials mostly change dramatically from those of their parent 3D materials [3, 4, 6, 10]. This stimulates application of 2D nanolayers of layered materials for development of devices with novel advanced characteristics in such areas as semiconductor electronics, electric batteries and supercapacitors [3, 4, 6], hydrogen generation, and CO₂ reduction and storage [6, 11].

In recent years, there is a growing interest in investigations of physicochemical properties (mechanical, electronic, optical, magnetic, adhesive, catalytic) of 2D layers and nanosheets particularly of metal diiodides $\text{M}_2\text{I}_2$ ($\text{M} = \text{Mg}, \text{Fe}, \text{Cd}, \text{Pb}$) with the crystallographic structure of different polytypes (2H, 4H, P6₃mc, etc) of the CdI₂ [12–18]. It was demonstrated both experimentally and theoretically that the mechanical [17, 19], electronic [13, 17], and optical [17] properties of metal diiodides are very sensitive to variation of the number of layers in nanosheets and considerably differ from those of the corresponding bulk compound. The technological success in preparation of 2D layers and nanolayers of metal diiodides via epitaxial deposition [12, 16–18] and exfoliation [3, 16] methods makes these compounds promising candidates for advanced applications in electronics [12], optoelectronics [12, 18], magnetoresistive spintronics [14], sensing, catalysis, and energy storage [5, 13].

Especially in applications of the exfoliation methods (through-solution, mechanical, intercalation) for preparation of 2D nanolayers of MI₂ layered compounds [2, 16, 19–21], it is of technological interest the
Theoretical quantification of the cohesive energy (intralayer and interlayer) both in 2D layers/nanolayers and parent 3D bulk crystals. In metal dihalides (MX$_2$) and particularly in MI$_2$ compounds, the chemical bonds are partially ionic and partially covalent, with dominating ionicity [22–28], and this results in dominating contribution of the Coulomb electrostatic energy to the total cohesive energy (cohesive energy includes also the repulsive, polarization, van der Waals, and covalent energies) [22–25, 29]. In its turn, the evaluation of the Coulomb electrostatic energy assumes, besides the partial (non-formal) ionic charges, also the precise knowledge of the Madelung constant, which characterizes the type of crystallographic arrangement of constituent ions in the crystal lattice [22, 24, 30].

There are two main approaches for calculation of the Madelung constant. The first approach assumes the direct summation in real space, and for this approach a number of effective methods have been proposed for achieving the fast convergence of the Madelung sum [31–34]. The second approach is more complex and is based on the Ewald’s method that assumes summation both in real and reciprocal spaces [35–37].

The Madelung constant ($A_M$) of metal dihalides (MX$_2$) and particularly of metal diiodides (MI$_2$), with the crystallographic structure of CdI$_2$ polytypes (2 H, 4 H, P6$_3$mc, etc.), is dependent on the three crystallographic lattice parameters: the lattice constants along the $a$ and $c$ crystallographic axes, $a$ and $c$, and the fractional out-of-plane coordinate $u$ of halogen ion (X) in a unit cell [24, 25, 29–38]. It is not a simple task to obtain an analytic dependence (i.e., analytic functional form) $A_M(a, c, u)$ from corresponding lattice summation. Therefore, in comparative analysis of the Madelung constants of different compounds, the dependence $A_M(a, c, u)$ is analyzed by calculating the numerical limit of the lattice sum (i.e., $A_M(a, c, u)$) for each compound of interest with the use of corresponding values of $(a, c, u)$ parameters [24, 30]. For CdI$_2$ type structure with a fixed parameter $u = 0.25$, a rather complex method for determining the functional dependence of the Madelung constant on $c/a$ ratio, $A_M(c/a, u = 0.25)$, was proposed by Herzig and Neckel [39]. However, in the case of compounds with parameters $u$ considerably deviating form a value $u = 0.25$, the above dependence cannot result in precise value for constant $A_M$, since $A_M$ is very sensitive to variations of the parameter $u$ [24, 29]. De Haan conducted a numerical analysis [40, 41] for the dependence of the Madelung constant of some metal dihalides MX$_2$, with CdI$_2$ (2 H polytype) structure, on the $c/a$ ratio and the geometrical parameter characterizing the degree of inclination of M-X bonds with respect to the crystallographic $c$ axis. Meanwhile, it would be useful, for 2D layers/nanolayers and parent 3D bulk crystals of metal diiodides (MI$_2$), to obtain the analytic dependence $A_M(a, c, u)$ incorporating also the dependence on parameter $u$. The knowledge of above analytic dependence $A_M(a, c, u)$ may considerably simplify the mathematical and physical analysis of the interdependence between the constant $A_M$ and lattice parameters. The analytic dependence $A_M(a, c, u)$ may be of a special interest also in high temperature [42, 43] and high pressure [44, 45] experiments, when the constant $A_M$ depending on temperature and/or pressure changes considerably.

Within the overall program of the study of structural, energy, and elastic characteristics of layered compounds, our previous publications [10, 46–48] were devoted to investigations of alkaline earth metal dihydroxides Mg(OH)$_2$ and Ca(OH)$_2$ [10, 46, 47] and iron diiodide FeI$_2$ [48] having CdI$_2$(2 H polytype) structure. In study [48], it is analyzed how under high-pressure conditions the variation of the pressure-dependent Madelung constant of the FeI$_2$ is associated with the structural phase transition of this compound. The most part of results in above studies [10, 47, 48] were obtained on the basis of the method for calculation of the Madelung lattice sums proposed in study [10]. The main idea of this approach is that, in the Madelung lattice sum, the summation is performed not over contributions corresponding to ‘ion-ion’ pair interactions, but over those corresponding to ‘molecule–molecule’ pair interactions (here, ‘molecule’ is defined through a formula unit MX$_2$, with M and X being a cation and an anion, respectively). Unlike the consideration of the ‘ion-ion’ pair interactions that result in conditional convergence of the lattice sum, the account of the ‘molecule–molecule’ interactions results in absolute and fast convergence of this sum. Therefore, it is of interest to apply this approach to 2D and 3D metal diiodides MI$_2$ with the CdI$_2$(2 H polytype) structure particularly for determination of the above specified analytic dependence $A_M(a, c, u)$ for the Madelung constant.

In this theoretical study, the Madelung constant ($A_M$) of metal diiodides MI$_2$ ($M =$ Mg, Ca, Mn, Fe, Cd, Pb) with CdI$_2$(2 H polytype) structure is calculated with the use of the approach proposed in author’s earlier work [10]. On the basis of the mathematical and graphical analysis of the dependence of the lattice sum (for constant $A_M$) on the crystallographic parameters $a$, $c$, and $u$, an analytic dependence $A_M(a, c, u)$ is obtained both for a 2D layer and parent 3D bulk crystal. The obtained analytic dependence $A_M(a, c, u)$ is also analyzed in terms of its (i) applicability to some other metal dihalides (MX$_2$) and metal dihydroxides [M(OH)$_2$] with the same polytypic structure, (ii) extreme values and character of variation depending on variation of individual crystallographic parameters $a$, $c$, and $u$, and (iii) validity for direct and precise analysis of the pressure-dependent variation of the Madelung constant.
2. **MI$_2$ compounds with CdI$_2$ (2 H polytype) structure**

The crystallographic structure of the 2 H polytype of metal diiodides MI$_2$ ($M = Mg, Ca, Mn, Fe, Cd, Pb$) is trigonal with space group $P\bar{3}m1$. In a MI$_2$ crystal, each positively charged metal (M) ion is octahedrally coordinated by the six nearest-neighbor iodine (I) ions in equal distances $R_\alpha (= R_{\alpha 1} = R_{\alpha 2})$ as shown in figures 1(a) and 1(b). These octahedral MI$_6$ complexes form ionic layers with (0001) orientation and stacking along the [0001] crystallographic direction (figure 1(c)). Each of these ionic layers is composed of the three ionic sublayers: a sublayer of M ions sandwiched between two sublayers of I ions (figure 1(c)). In above all three sublayers, the ions are arranged with a hexagonal close-packed configuration as depicted in figure 1(d). The physical rectangular coordinate system, $x$ $y$ $z$, is chosen in such a way that the $x$, $y$, and $z$ axes are parallel to [1210], [0001], and [1010] crystallographic directions, respectively, the $x$ $z$ coordinate plane coincides with position of a sublayer of M ions (figure 1(c)). The above specified [1210] and [0001] directions define the crystallographic $a$ and $c$ axes, respectively. The $a$ and $c$ lattice parameters are shown in figures 1(c) and (d). The fractional out-of-plane coordinate $u$ of iodine ion in a unit cell is defined as the ratio $u = h/c$, where $h$ is the distance between the sublayer of M ions and sublayers of I ions in an individual MI$_2$ layer, resulting in thickness $2h$ of the layer (figure 1(c)).

3. **Results and discussion**

3.1. **Calculation of the Madelung constant for 3D bulk crystal and a 2D layer of MI$_2$ compounds**

The Coulomb energy of electrostatic interaction per molecule in a 3D bulk crystal of ionic binary compound MX$_2$ is expressed as
where \( Z_e \) and \( Z_a \) are the absolute values of partial (or equivalently, fractional) charges on cations M and anions X, respectively (\( Z_e = 2 \), \( Z_a \) = 1.602 \times 10^{-19} \text{C} \) is the absolute value of the electron charge, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{C}^2 \text{m}^{-1} \text{kg}^{-1} \text{V}^{-1} \text{m}^{-1} \) is the permittivity of vacuum, \( R \) is the nearest-neighbor interionic distance \( M - X \), and \( A_M \) is the Madelung constant. As mentioned above, in metal dihalides (MX2) and particularly in MI2 compounds, the chemical bonds are partially ionic and partially covalent [22–28]. Therefore, in equation (1), the charge numbers \( Z_e \) and \( Z_a \) are fractional and do not coincide with (are smaller than) their corresponding formal values \( Z_e = 2 \) and \( Z_a = 1 \). The data for the Madelung constants of metal diiodides MI2 (M = Mg, Ca, Mn, Fe, Cd, Pb), with CdI2 (2 H polytype) structure, are available in a number of publications [24, 29, 30, 39–41]. However, the parameter \( N \) for different MI2 compounds was calculated by applying alternative methods, with different precisions. For correctness of the comparative analysis it is necessary that the parameters \( A_M \) for these compounds were evaluated by the same method. Therefore, for this purpose, in the present study it is used the approach proposed in author’s earlier work [10]. This approach has been proposed for calculation of the Madelung constant associated with the Coulomb energy of interaction of an adsorbed \( \text{Ca(OH)_2} \) molecule with constituent ions of a \( \text{Ca(OH)_2} \) crystal. The \( \text{Ca(OH)_2} \) is isostuctural with the 2 H polytype of CdI2, and this enables to apply the above approach in the calculations of the Madelung constants of MI2 compounds. As it was mentioned in section 1, the main idea of this approach is that, in the Madelung lattice sum, the summation is performed not over contributions corresponding to ‘ion-ion’ pair interactions (in this case, the convergence of the lattice sum is conditional), but over those corresponding to ‘molecule-molecule’ pair interactions schematically shown in figure S1 of Supplementary material (is available online at stacks.iop.org/MRX/7/026301/mmedia). The summation in real space by means of account of ‘molecule-molecule’ pair interactions results in absolute and fast convergence of the Madelung lattice sum. Because of a high symmetry in the mutual coordination of unlike constituent ions in MI2 complexes (figure 1(a)), the configuration of a MI2 molecule cannot be defined uniquely and may be chosen in many ways; two possible molecular configurations, straight \( \text{I(1)} - \text{M} - \text{I(2)} \) and bent \( \text{I(1)}^+ - \text{M} - \text{I(2)} \) configurations, are shown in figure 1(a). As in previous work [10], the former configuration is used (for definiteness and convenience) in present study in the calculations of the Madelung constant. Molecules in the MI2 crystal with above specified straight \( \text{I(1)} - \text{M} - \text{I(2)} \) configuration, are shown in ball-and-stick presentation in figures 1(c) and (d). For convenience of readers, the most important details of calculations of the Madelung constant of MI2 (M = Mg, Ca, Mn, Fe, Cd, Pb) compounds are represented from study [10] in section 1 of Supplementary material. For the Madelung constant \( A_M \) in equation (1), these calculations result in expression

\[
A_M = A_o + \frac{1}{2}(A_1 + A_2 + A_3),
\]

where the constant \( A_o (= 1.75) \) is the contribution resultant from intramolecular \( \text{M} - \text{I(1)}, \text{M} - \text{I(2)}, \) and \( \text{I(1)} - \text{I(2)} \) Coulomb pair interactions of ions in MI2 reference molecule with position \( (n = 0, m = 0, l = 0) \) (figures 1(c) and (d)), \( A_1 \) is the contribution resultant from Coulomb pair interactions of the reference molecule with the 1D chain of molecules situated along the x coordinate axis (figures 1(c) and (d)), \( A_2 \) is the contribution resultant from Coulomb pair interactions of the reference molecule with the molecules in 2D molecular layer with \( m = 0 \), except with those belonging to above specified 1D molecular chain (figure 1(d)), and \( A_3 \) is the contribution resultant from Coulomb pair interactions of the reference molecule with molecules in the 3D crystal, except with those belonging to above specified 2D molecular layer with \( m = 0 \) (figure 1(c)). From practical standpoint, it is also important to evaluate the intralayer Coulomb energy, i.e. the contribution of 2D layer into the total energy \( U_C \) expressed via equations (1) and (2). The above contribution is obtained from equations (1) and (2) by substitution \( A_3 = 0 \) into equation (2) (i.e., the interlayer interaction is excluded):

\[
U_C = \frac{-Z_e Z_a e^2}{4\pi\varepsilon_0 R} A_{ML},
\]

\[
A_{ML} = A_o + \frac{1}{2}(A_1 + A_2),
\]

where \( A_{ML} \) and \( U_C \) are the Madelung constant and Coulomb energy of a 2D layer per molecule, respectively. The numerical data for contributions \( A_o, A_2, \) and \( A_3 \) to the Madelung constants \( A_M \) and \( A_{ML} \) in equations (2) and (4) are obtained from equations (S5), (S7), and (S9) of Supplementary material with the use of the data for \( \{a, c, u\} \) parameters listed in table 1. The lattice summations according to equations (S5), (S7), and (S9) are performed with the use of the program Mathematica (Wolfram Research, Inc., https://www.wolfram.com). The calculated data of \( \{A_o, A_2, A_3\} \) contributions and \( \{A_M, A_{ML}\} \) constants for MI2 compounds are presented in in table A1 of the appendix and table 1, respectively, and were achieved for summation limits with \( k = 60 \) (for definition of \( k \) see section 3.2). In table 1, for MI2 compounds the data are listed in the order of increase of the Madelung constant \( A_M \). For MI2 (M = Mn, Fe, Cd, Pb) compounds, table 2 compares the \( A_M \) and \( A_{ML} \) data obtained in this study with those reported in literature [24, 41] and shows a satisfactory agreement within the
prescribed accuracy of $\sim 10^{-4}$. According to the data presented in table 1, for all MI$_2$ compounds, $A_M$ exceeds $A_{ML}$ only by a small value that is much less than 1%. Such a type relationship between $A_M$ and $A_{ML}$ results from the data of their components $A_1$, $A_2$, and $A_3$ (see equations (2) and (4)) presented in table A1 of the appendix, according to which $A_1 > A_2 > A_3$. This means that, in layered MI$_2$ compounds, the Coulomb intralayer interaction drastically exceeds the interlayer interaction, and this result is typical of ionic layered compounds with different crystallographic structures [40, 41] and predicts a high structural stability for their free standing/exfoliated 2D layers.

It should be noted that, in above cited publications [22, 24, 29, 40, 41] reporting the data for the Madelung constant, equation (1) is expressed in other form in terms of the definition of the Madelung constant:

$$U = -\frac{Z_2}{4\pi\varepsilon_0 R} A_M^2,$$

where $A_M = 2 A_M$. Equation (5) is obtained form equation (1) with the use of the relationship $Z_e = 2 Z_a$ and incorporation of the factor 2 into the Madelung constant $A_M$. In the case of definition of the Madelung constant via equation (5), the similar relationship holds for the Madelung constant of an individual layer, $A_{ML}$, in which it is assumed that $A_{ML}$ is introduced by equation (3). In this study, it is preferred to define the Madelung constant ($A_M$) via equation (1) since, unlike the Madelung constant ($A_M$) in equation (5), the constant $A_M$ in

| Compound | $a$ (Å) | $c$ (Å) | $u$ | $f^*$ | $\lambda_M^a$ | $\lambda_M^{an}$ | $A_M$ | $A_{ML}$ | $A_{ML,a}$ |
|----------|---------|---------|-----|-------|-------------|-------------|-------|----------|-----------|
| FeI$_2$  | 4.040$^a$ | 6.750$^a$ | 0.250$^a$ | 2.394 | 2.162 | 2.163 | 2.160 | 2.160 |
| PbI$_2$  | 4.558$^b$ | 6.986$^b$ | 0.268$^b$ | 2.435 | 2.180 | 2.178 | 2.175 | 2.175 |
| MnI$_2$  | 4.146$^c$ | 6.829$^c$ | 0.245$^c$ | 2.478 | 2.192 | 2.192 | 2.190 | 2.190 |
| CdI$_2$  | 4.490$^d$ | 6.975$^d$ | 0.250$^d$ | 2.575 | 2.222 | 2.222 | 2.219 | 2.219 |
| VCl$_2$  | 3.601$^e$ | 5.835$^e$ | 0.250$^e$ | 2.468 | 2.189 | 2.189 | 2.189 |
| FeBr$_2$ | 3.776$^f$ | 6.227$^f$ | 0.238$^f$ | 2.548 | 2.213 | 2.213 | 2.214 |
| Mg(OH)$_2$ | 3.142$^g$ | 4.766$^g$ | 0.222$^g$ | 2.970 | 2.301 | 2.301 | 2.292 |
| Co(OH)$_2$ | 3.182$^h$ | 4.651$^h$ | 0.225$^h$ | 3.041 | 2.311 | 2.311 | 2.297 |

* [44].
† [49].
‡ [50].
§ [40].
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‖ [51].
‖‖ the data determined from equation (7).
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Table 2. Comparison of the data for the Madelung constants $A_M$ and $A_{ML}$ reported in literature and obtained in this work from lattice sums according to equations (2) and (4), respectively.

| Compound | Cdl$_2$ | PbI$_2$ | MnI$_2$ | FeI$_2$ |
|----------|---------|---------|---------|---------|
| $A_M$    | 2.194$^a$ | 2.183$^a$ | 2.179$^b$ | 2.163$^b$ |
| $A_{ML}$ | 2.192$^c$ | 2.178$^d$ | 2.192$^e$ | 2.162$^f$ |

* [41].
† [24].
‡ this work.
equation (1) does not incorporate any parameter associated with the ionic charges and solely is dependent on the geometry of ionic arrangement (i.e., on the crystallographic parameters). It should be clarified that, in table 2, the literature data [24, 41] for constants \( A_M \) and \( A_{ML} \) are given in terms of equations (1) and (3), respectively.

3.2. Analytic dependence of the Madelung constant on the crystallographic parameters for 3D bulk crystal and a 2D layer

According to analysis presented in section 2 of Supplementary material, it is expected that the analytic dependence of the Madelung constants \( A_M \) and \( A_{ML} \) on the crystallographic parameters \( a, c, \) and \( u \) may be expressed, with a high approximation, solely by the ratio of parameter \( a,u \) and product \( c, a/u \). In order to achieve this analytic dependence, first, the plot of \( A_M \) against parameter \( a/(u \ c) \) was performed with the use of the data \{a, c, u, \( A_M \)\} of MI2 compounds presented in table 1. This plot is presented in figure 2(a) via red solid circles and shows a smooth monotonic increase of the constant \( A_M \) with increase of the parameter \( a/(u \ c) \) (at the top of this figure, the MI2 compounds are listed in the order of increase of the constant \( A_M \)). Next, the best fit (interpolation curve) to \{\( a/(u \ c), A_M \)\} data points was determined as the following quadratic function:

\[
A_{M, an} = k_1 f^2 + k_2 f + k_3,
\]

where

\[
f = a/(uc),
\]

\( k_1 = -0.2516, k_2 = 1.5741, \) and \( k_3 = -0.1631 \) (in figure 2(a), this interpolation curve is shown as a solid curve). Parameter \( f \) (defined via equation (7)) is not of a formal character and possesses a geometrical meaning. As seen in figures 1(a) and (c), the ratio \( a/(u \ c) \), with taking account of the relationship \( h = u \ c \) (see section 2), may serve as a measure of the flatness of FeI\(_6\) octahedral complexes in layers of a FeI\(_2\) crystal in the [0001] direction (i.e., along the crystallographic c axis). The larger is the flatter are FeI\(_6\) octahedral complexes (i.e., FeI\(_2\) layers). Accordingly, parameter \( f \) given by equation (7) may be defined as the ‘flatness parameter’ and is used in further presentation of results instead of the ratio \( a/(u \ c) \). Equation (6) may be qualified as an approximate analytic dependence of the Madelung constant on \{a, c, u\} parameters, and the subindex ‘an’ in the notation \( A_{M, an} \) is introduced in order to distinguish the approximated values \( A_{M, an} \) of the Madelung constant from

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**Figure 2.** (a) The plot of the Madelung constant \( A_M \) against the flatness parameter \( f \) (red solid circles) for MI\(_2\) compounds (at the top of figure, the MI\(_2\) compounds are listed in the order of increase of \( A_M \)). The interpolation curve (solid curve) to \{\( f, A_M \)\} data points of MI\(_2\) compounds plotted according to equation (6). The black solid triangles present the plot of \{\( f, A_M \)\} data points for VCl\(_2\) and FeBr\(_2\) compounds. (b) The plots of figure (a) in a wider range of variation of the parameter \( f \) that contains the \{\( f, A_M \)\} data points for compounds Mg(OH)\(_2\), and Co(OH)\(_2\) (black solid triangles shown by arrows). (c) The dependence of the Madelung constant \( A_M \) of MI\(_2\) compounds on the ratio \( c/a \) (at the top of figure, the MI\(_2\) compounds are listed in the order of increase of the ratio \( c/a \)). (d) Convergence of partial lattice sums \( A_{M, an} \) and \( A_{ML, an} \) to their corresponding limits \( A_M = 2.222 \) and \( A_{ML} = 2.219 \) for the CaI\(_2\) compound.
corresponding precise values $A_M$ obtained from the lattice summation method according to equation (2). To check how precise is equation (6) for calculation of the Madelung constant of MI$_2$ compounds, table 1 compares the values $A_M$ obtained from lattice summation (equation (2)) with the corresponding values $A_{M,acu}$ calculated by equation (6) with the use of [a, c, u] parameters from table 1. The difference in these values is within the range of 0.01% and such a high precision confirms the validity of equation (6). To check the applicability of the dependence given by equation (6) to other metal dihalides (MI$_2$) with CdI$_2$ (2 H polytype) structure, equation (6) was used for calculation of the Madelung constants of the two such a type compounds, VCl$_2$ and FeBr$_2$. With the use of the [a, c, u] data of VCl$_2$ and FeBr$_2$ given in table 1, equation (6) results correspondingly in $A_{M,acu}$ values 2.189 and 2.214 which are in very good agreement with the corresponding $A_M$ values 2.189 and 2.213 calculated according to equation (2) (see table 1 and figure 2(a)). Note that the above satisfactory agreement was achieved in spite of the [$f$, $A_M$] data points of VCl$_2$ and FeBr$_2$ were not used in obtaining of equation (6). Nevertheless, this agreement could be expected since, both for VCl$_2$ and FeBr$_2$, the value of parameter $f$ is within the range of variation of this parameter for MI$_2$ compounds (figure 2(a)). In this context, it was of interest to check the applicability of equation (6) to compounds, with the CdI$_2$ (2 H polytype) structure, having distant values of $f$ with respect to the range of variation of the parameter $f$ of MI$_2$ compounds. Particularly, for the metal dihydroxides Mg(OH)$_2$ and Co(OH)$_2$ with CdI$_2$ (2 H polytype) structure, parameter $f$ accepts correspondingly the values 2.970 and 3.041 calculated with the use of the corresponding [a, c, u] data given in table 1. The above values, 2.970 and 3.041, are considerably distant from the range of variation of the parameter $f$ for MI$_2$ compounds, 2.394 < $f$ < 2.575. Figure 2(b) reproduces the plots of figure 2(a) in a wider range of variation of the parameter $f$ and also incorporates the data points [$f$, $A_M$] for compounds Mg(OH)$_2$ and Co(OH)$_2$ (black solid triangles shown in figure by arrows) with a slight but distinguishable deviation from positions of corresponding [$f$, $A_{M,acu}$] data points (i.e., from interpolation curve). For Mg(OH)$_2$ and Co(OH)$_2$, the relative difference between the corresponding values $A_M$ and $A_{M,acu}$ given in table 1 is sufficiently small, 0.4% and 0.6%, respectively. This means that, the analytic dependence $A_{M,acu}(f)$ given by equation (6) is applicable with accuracy ~0.5% at least up to values $\approx$3 of the flatness parameter $f$.

Similarly to the approach in obtaining the equation (6), the data [a, c, u, $A_{M,acu}$] of MI$_2$ compounds presented in table 1 result in corresponding analytic dependence for the Madelung constant of a 2D layer comprised in a 3D crystal:

$$A_{M,acu} = q_1 f^2 + q_2 f + q_3,$$

where $f$ is expressed via equation (7), $q_1 = -0.325414$, $q_2 = 1.9437$, and $q_3 = -0.628248$. To check how precise is equation (8) for calculation of the Madelung constant of MI$_2$ compounds, table 1 and figure 3 compare the values $A_M$ obtained from lattice summation [equation (4)] with the corresponding values $A_{M,acu}$ calculated by equation (8) with the use of [a, c, u] parameters from table 1. The obtained data show that, for all compounds, there is no difference between the corresponding values of constants $A_{M}$ and $A_{M,acu}$ within the prescribed accuracy. In the whole range of variation of the parameter $f$ for MI$_2$ compounds, 2.394 < $f$ < 2.575, the dependence given by equation (8) is very close to that given by equation (6) as a result of the relationship $A_{M,acu} = A_{M,acu} \approx 0.5A_1 \sim 10^{-3}$ (this is understood from equations (2) and (4) and the data for contribution $A_1$ presented in table A1 of the appendix). For a free standing or an exfoliated layer of a layered compound (particularly, of MI$_2$ compounds), the lattice parameter $a$ preserves its physical and crystallographic meaning, whereas the lattice parameter $c$ is meaningless (figure 1(c)). Therefore, in this case, parameter $f$ associated with equation (8) may be expressed as $a/h$ with the use of the definition $u = h/c$ introduced in section 2 (parameter $h$ is the half thickness of a MI$_2$ layer as shown in figure 1(c)). The results of atomistic simulation [55] show that, for MI$_2$ compounds, parameters $a$ and $h$ do not practically differ from their corresponding bulk values. In the case of experimental confirmation of the above theoretical finding [55], equation (6) with parameter $f$ defined as $f = a/h$ may be also applicable with a good approximation to free standing/exfoliated layers of MI$_2$ compounds. Figure 2(c) presents the dependence of the Madelung constant $A_M$ of MI$_2$ compounds on the ratio $c/a$ that is mostly used in literature in the analysis of the character of variation of $A_M$ versus lattice parameters $a$ and $c$ [24, 30, 39, 41]. In spite of parameter $u$ in MI$_2$ compounds varies in a narrow range 2.242 < $u$ < 2.268 (table 1), the comparison of the plot [$f$, $A_M$] (i.e., of the plot [$a/(uc)$, $A_M$]) in figure 2(a) (red solid circles) with the plot [$c/au$, $A_M$] in figure 2(c) shows that the character of variation of the constant $A_M$ in the plot [$a/(uc)$, $A_M$] (figure 2(a)) is strongly influenced by the parameter $a$. This necessitates in the analysis of the dependence $A_M(a, c, u)$ to use accurate values for parameter $u$. It is also important to note that unlike the monotonous dependence [$a/(uc)$, $A_M$] (figure 2(a)), in the dependence [$c/au$, $A_M$] (figure 2(c)) with missing parameter $u$, the character of variation of $A_M$ with ratio $c/a$ is random and cannot be interpreted in any obvious way.

It is of interest, for MI$_2$ compounds, to analyze the convergence of lattice sums in the determination of the Madelung constants of 3D bulk crystal and a 2D layer, $A_M$ and $A_{ML}$. As a representative example, figure 2(d) shows for calcium diiodide (CaI$_2$) the convergence of partial lattice sums $A_{ML}$ and $A_{ML}$ to their corresponding
limits $A_M$ and $A_{ML,k}$, where the subindex $k$ stands for positive integers $k(=1, 2, 3,...)$ that define the limits of summation over intervals $-k \leq n \leq k$, $-k \leq l \leq k$, and $-k \leq m \leq k$ according to equations (S5), (S7), and (S9) of Supplementary material. This corresponds to summation over cubic extensions. It should be detailed that, according to equations (2) and (4), the partial sums $A_{M,k}$ and $A_{ML,k}$ are defined as $A_{M,k} = A_0 + 0.5\left(a_{1,k} + a_{2,k} + a_{3,k}\right)$ and $A_{ML,k} = A_0 + 0.5\left(a_{1,k} + a_{2,k}\right)$, respectively, where the partial sum $A_{i,k}$ relates to $A_i$ contribution ($i = 1, 2, 3$). The plots in figure 2(d) show a monotonous and rapid convergence of the partial lattice sums $A_{M,k}$ and $A_{ML,k}$ in the interval $1 \leq k \leq 20$. For prescribed accuracy of $\sim 10^{-4}$, $A_{M,k}$ and $A_{ML,k}$ reach the corresponding limits $A_{M} = 2.222$ and $A_{ML} = 2.219$ at $k = 15$ and 7, respectively. This means that, for MI$_2$ compounds, the Coulomb energy of 3D nanocrystals in comparison to that of 2D nanolayers (here, it is implied that the 2D layer is nanosized also in in-plane directions) is influenced by the size effect in a higher degree.

Equation (6) enables directly and simply to specify the trends of variation of the Madelung constant with variation of the structural parameters $a, c$, and $u$. In the range of variation of the flatness parameter $f$ for compounds listed in table 1, $2.394 < f < 3.041$, the dependence given by equation (6) (see figures 2(a) and (b)) and equation (7) result in the following important conclusions: (i) at a fixed $u$, the Madelung constant increases with increase of the ratio $a/c$, (ii) at a fixed product $u \times c$, i.e., at a fixed thickness of layers 2 $h$ (see section 2 and figure 1(c)), the Madelung constant increases with increase of the lattice parameter $a$, and (iii) at a fixed ratio $a/c$, the Madelung constant increases with decrease of the parameter $u$. The above trends are confirmed by the proposed lattice summation method and remain in force in the case of analytic dependence given by equation (8) for the Madelung constant of a 2D layer.

In the dependence given by equation (6), the maximal value of the Madelung constant with respect to parameter $f$, $A_{ML,max} = 2.299$, is achieved at $f = 3.128$, and these data show that the Madelung constants of the compounds Mg(OH)$_2$ and Co(OH)$_2$ are on maximal level (see table 1 and figure 2(b)). Correspondingly, in the dependence given by equation (8), the maximal value, $A_{ML,max} = 2.274$, is achieved at flatness parameter $f = 2.987$.

3.3. Applicability of the analytic dependence $A_{ML,an}(f)$ to high-pressure structural states

The aim of this section is to demonstrate that that analytic dependence $A_{ML,an}(f)$ given by equation (6) is also valid for calculation (tracing of variation) of the Madelung constant of MI$_2$ compounds under high-pressure conditions.

With the use of the experimental results reported in literature [44], in author’s recent study [48] it is demonstrated that equation (6) with coefficients $k_1 = -0.251642, k_2 = 1.574089$, and $k_3 = -0.163095$ is also valid to a high approximation for calculation of the Madelung constant of FeI$_2$ at high hydrostatic pressures.

Note that the above coefficients practically coincide with those achieved in this study: $k_1 = -0.2516$, $k_2 = 1.5741$, and $k_3 = -0.1631$ (see section 3.2). Table A2 of the appendix presents: (i) the data of the lattice parameters $(a, c, u)$ of FeI$_2$ measured in above mentioned experimental study [44] by x-ray diffraction technique at ambient pressure ($\sim 0$ GPa) and at different values of the applied hydrostatic pressure $P = 4, 7.8, 12.5, 16.9$ GPa and (ii) the data for the flatness parameter $f$ and the Madelung constant $A_M$ calculated correspondingly according to equations (7) and (2) with the use of above experimental data $(a, c, u)$ [44]. With the use of the data from table A2, figure 4 presents for FeI$_2$ the plot of the Madelung constant $A_M$ versus the
flatness parameter $f$ at ambient pressure, $\approx 0$ GPa, and applied pressures $P = 4, 7.8, 12.5$, and $16.9$ GPa (black triangles). Figure 4 also shows (i) the plot of the data points $\{f, A_M\}$ for MI$_2$ (M = Pb, Mn, Cd, Mg, Ca) compounds at ambient pressure according to data from table 1 (red dots) and (ii) the plot of the analytic dependence $A_{M,an}(f)$ given by equation (6) (the above indicated plots $\{f, A_M\}$ and $A_{M,an}(f)$ are also presented in figure 2(a)). The plots in figure 4 show that under high-pressure conditions the analytic dependence $A_{M,an}(f)$ given by equation (6) very well reproduces the pressure-dependent variation of the Madelung constant $A_M$ calculated from the lattice sums according to equation (2) (see black triangles in this figure). To check how precise is equation (6), table A2 of the appendix compares for all applied pressures the values $A_M$ obtained from lattice summation [equation (2)] with the corresponding values $A_{M,an}$ calculated by the analytic dependence given by equation (6). The difference in these values is within the range of $0$–$0.1\%$, and such a high precision confirms the validity of equation (6) in high-pressure experimental investigations. Besides, the data in table A2 show that the Madelung constant varies with pressure within a rather broad range of $2.081$–$2.191$. According to results obtained in above mentioned publications [44, 48], equation (6) also predicts the minimization of the Madelung constant $A_M$ at the pressure $16.9$ GPa of the structural phase transition of FeI$_2$ (see figure 4).

Thus, equation (6) enables directly and precisely to quantify the variation of the Madelung constant of FeI$_2$ depending on pressure with no need in calculations of lattice sums. It is expected that equation (6) is also valid for precise analysis of the pressure-induced variations of the Madelung constant of metal diiodides MI$_2$ (M = Pb, Mn, Cd, Mg, Ca). Our preliminary theoretical analysis of the high pressure experimental results, reported in literature for metal dihydroxides with the CdI$_2$ (2H-polytype) such as Mg(OH)$_2$ [56], Ca(OH)$_2$ [57], and Co(OH)$_2$ [58], show that equation (6), with slightly corrected coefficients $k_1$, $k_2$, and $k_3$, is also applicable to analysis of high-pressure dependent variations of the Madelung constant of these compounds. The results associated with above analysis will be published in our next work.

4. Conclusion

For metal diiodites (MI$_2$) with CdI$_2$ (2H-polytype) structure, an analytic dependence of the Madelung constant on the crystallographic parameters is obtained both for a 2D layer and 3D bulk crystal of these compounds. It is shown that this analytic dependence (i) reproduces with accuracy of $0$–$0.1\%$ the Madelung constants of MI$_2$ compounds determined from lattice summation, (ii) is also applicable with a high accuracy to other metal dihalides and metal hydroxides, with CdI$_2$ (2H-polytype) structure, in the variation range of the flatness parameter $f$ up to values $\approx 3$, and (iii) is very sensitive with respect to variation of the unit cell parameter $u$. Both the Madelung constants of a 2D layer and 3D bulk crystal of MI$_2$ compounds, $A_M$ and $A_{M,an}$, increase in the order FeI$_2$ $<$ PbI$_2$ $<$ MnI$_2$ $<$ CdI$_2$ $<$ MgI$_2$ $<$ CaI$_2$.

The results reported in this study may be useful in the analysis of structural changes and phase transitions in high-pressure experimental investigations of metal diiodides.

The analytic dependence $A_M(a, c, u)$ may be incorporated into atomistic simulation programs for modeling of the cohesive energy and determination of the equilibrium crystallographic parameters $a$, $c$, and $u$ when account of the contribution of the Coulomb energy is necessitated.
Appendix

Table A1 lists the contributions $A_1$, $A_2$, and $A_3$ to the Madelung constant $A$ in equation (2). The contributions $A_1$, $A_2$, and $A_3$ are determined correspondingly from the lattice sums given by equations (55), (57), and (59) of Supplementary material.

| Compound | $A_1$  | $A_2$  | $A_3$  |
|----------|--------|--------|--------|
| FeI$_2$  | 0.570  | 0.251  | 0.0038 |
| PbI$_2$  | 0.582  | 0.268  | 0.0090 |
| MnI$_2$  | 0.594  | 0.286  | 0.0035 |
| CdI$_2$  | 0.596  | 0.288  | 0.0043 |
| MgI$_2$  | 0.601  | 0.294  | 0.0032 |
| CaI$_2$  | 0.619  | 0.320  | 0.0052 |

Table A2. The data $\{a, c, u\}$ obtained for FeI$_2$ in study [44] from XRD measurements at different hydrostatic pressures $P$, the data of the flatness parameter $f$, calculated from equation (7) with the use of the data $\{a, c, u\}$, and the Madelung constants $A_M$ and $A_M^{\text{calc}}$, calculated according to equations (5) and (6), respectively, with the use of the data $\{a, c, u\}$.

| $P$ (GPa) | $a$ (Å) | $c$ (Å) | $u$  | $f$  | $A_M$  | $A_M^{\text{calc}}$ |
|-----------|----------|----------|------|------|--------|---------------------|
| $\approx$0 | 4.040    | 6.750    | 0.250| 2.394| 2.162  | 2.163              |
| 4.0       | 3.926    | 6.249    | 0.254| 2.473| 2.191  | 2.191              |
| 7.8       | 3.855    | 6.057    | 0.275| 2.314| 2.133  | 2.132              |
| 12.5      | 3.788    | 5.919    | 0.282| 2.269| 2.114  | 2.113              |
| 16.9      | 3.671    | 5.842    | 0.286| 2.197| 2.078  | 2.081              |

ORCID iDs

V S Harutyunyan  
https://orcid.org/0000-0002-8015-5891

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