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Jahn-Teller Effect on Binary Indium Bromide — An *Ab Initio* Study

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Abstract: In order to elucidate the unusual chemical sensitivity of binary indium bromides, the potential energy surface of the model complex $InBr_8^{7-}$ has been studied by means of *ab initio* all-electron calculation with larger basis sets. The configuration is on a local maximum of the energy surface and crystal potential around In^+ is soft, allowing small spontaneous distortions as a result of a second-order Jahn-Teller instability.

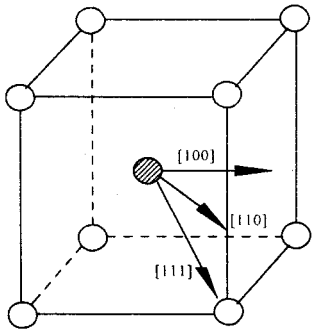
Keywords: Binary indium bromides, *ab initio* calculation, potential energy curve, second-order Jahn-Teller effect.

Among indium halides, the structural chemistry of the bromides is richest. While the first study can trace back to the beginning of the century[1], the binary phase diagram has only recently been completed[2-4] due to the unusual instability of this compounds like InBr, In_5Br_7, In_2Br_3, In_4Br_7 and $InBr_2$. According to the experiment, the binary indium bromides are very sensitive to the air, light, humidity and mechanical stress. The origin of the unusual instability of the compounds created great interest among the theoretical chemists. The results based on the semi-empirical quantum chemical calculations are argued [5], while the recent all-electron *ab initio* studies was not able to present in-depth description of the potential energy surface of the compounds because of the small basis sets [6]. In this paper, we adopt larger basis sets in the all-electron *ab initio* studies to investigate the potential energy surface and molecular orbital properties in order to elucidate the structural instability of binary indium bromides. This may be helpful to the inorganic solid state synthesis.

The *ab initio* calculations are performed with GAUSSIAN 98 package[7]. We take a cubic $InBr_8^{7-}$ polyhedron (**Figure 1**) as the model, which is found in $InBr_2$ compound. At beginning, In^+ –Br^- bond length is set to 345 pico-meter (pm), similar to the actual value of $InBr_2$ crystal. In order to sample points of the potential energy surface, we then let In^+ ion move in three different directions, namely the four-, two-, three-fold rotational axes, up to 35 pm. The eight bromide atoms are kept frozen at their original positions since the latter are typically determined by the remaining three dimensional network consisting of others, much more strongly bonded subunits. Thus, there is no need to optimize the bond lengths of above polyhedron. The total energy is calculated at the 3-21G* level for indium

atom and 6-311G* for bromide atoms. Totally there are 451 basis functions. Accordong to our previous studies, the electron correlation effect was not critical to the local minimum on potential energy surface for this polyhedron [6].

Figure 1. Configuration of cubic $InBr_8^{7-}$ eight coordination polyhedron in $InBr_2$ crystal



The calculated potential energy curves for the InBr87- polyhedron is depicted in Figure 2. Figure 2(a) reveals that the starting cubic structure with monovalent indium at the very center is a local energy maximum that may be slightly lowered when In+ moves away from its primary position along any one of the three high symmetry directions. Thus, The cubic InBr87- entity is intrinsically unstable.

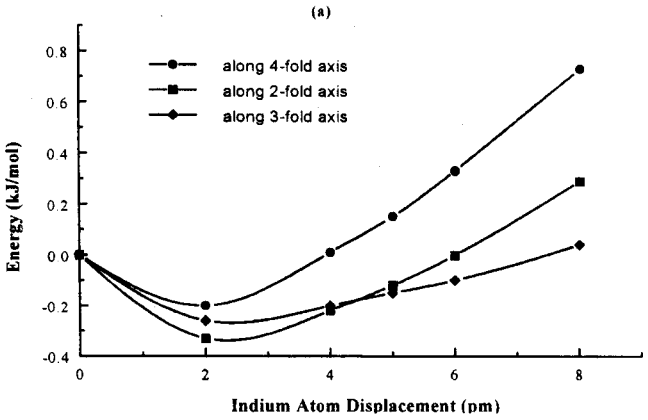
A local minimum is achieved on the potential energy curve when In+ is dislocated by about 2-3 pm depends on the moving directions. However the energy gains are extraordinarily small of about 0.15 – 0.35 kJ/mol. Prior semi-empirical calculation could not obtain so tiny energy gains and thus resulted in mistaken conclusion, while the ab initio calculation with smaller basis set overestimated both energy gains and geometric distortion.

However, independent from these quantitative considerations, it is clear that the potential around the central indium is very flat and changes smoothly as shown in Figure 2(b). When indium atom distorts 30 pm from primary position, the energy changes about 4.5 kJ/mol along four-fold axis direction, 10 kJ/mol along 2-fold axis direction and 16 kJ/mol along 3-fold axis direction. The force constant analysis also shows the crystal potential around central indium atom is very soft. Besides that, the energy curves along the different principle directions are quite different, indicating that the potential energy distribution around In+ is anisotropic. The most flat direction is along four-fold axis. The Mulliken population analysis shows the s/p mixing of indium when In+ moves away from the central position. For example, the population of 5s orbital of indium reduces from 1.995 to 1.990 while that of 5p orbital increases from 0.095 to 0.110 when indium atom moves 30 pm away along the four-fold axis. Consequently, such a rehybridization due to a Jahn-Teller effect of second order is shifting electronic charge from the indium 5s orbital into the indium 5p orbital.

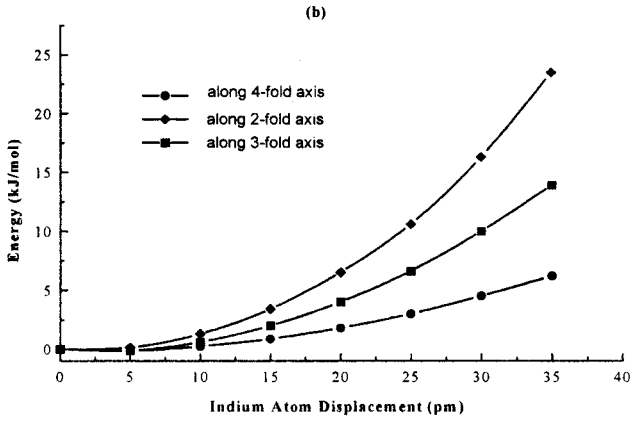
In summary, the InBr87- cubic polyhedron is an instinctively unstable configuration. The corresponding solid state compounds show an unusual Jahn-Teller effect of second-

order; The potential energy curve around central indium is very flat cause the strong tendency of distortion which will results in the sensitivity of compounds to air, light, humidity and mechanical stress; The potential energy distribution around the cubic center is anisotropic, which means the decomposed products of the compounds are fixed. This agrees with the experimental results. It has already been reported experimentally that the twelve-fold coordination polyhedron found in In4Br7 binary indium bromide has a distortion of In+ of about 40 pm in the low-temperature crystallographic measurement 8. We hope the eight-fold coordination polyhedron distortion predicted in this paper may also be found in further experiments.

Figure 2 Potential energy curves of the $InBr_8^{7-}$ polyhedron.



(a) Potential energy curve of an $InBr_8^{7-}$ polyhedron, the In^+ ion moving along the four-, two- and three-fold symmetry axis from 0 – 8 pm



(b) Same as (a) but x axis region is from 0 – 40 pm.

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