First-Principles Study of Spontaneous Polarization in Tetrathiafulvalene-p-Chloranil (TTF-CA)

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The organic compound tetrathiafulvalene-p-chloranil (TTF-CA; TTF = C\textsubscript{6}H\textsubscript{4}S\textsubscript{4}, CA = C\textsubscript{6}Cl\textsubscript{4}O\textsubscript{2}) has been attracting much attention because of its peculiar phase transition and related phenomena. TTF-CA belongs to a class of materials called mixed-stack compounds. They fall into two types depending on the balance between the ionization cost and the electrostatic energy. One is a neutral donor-acceptor complex whose constituent molecules are nominally neutral. The other is an ionic salt composed of donors and acceptors. Several mixed-stack compounds are located near the neutral-ionic phase boundary and undergo a phase transition by applying pressure or decreasing temperature. TTF-CA is a typical example. At room temperature and ambient pressure, TTF-CA is in the neutral (N) phase. The system becomes the ionic (I) phase above \sim 11 kbar at 300 K or below \sim 84 K at ambient pressure. In the I phase, donor-acceptor dimers with weak bond are formed along the stacking direction \(a\) and the inversion symmetry is lost for the crystal and for each molecule. As a result, the I phase is ferroelectric while the N phase is paraelectric.

In the present work, we have evaluated spontaneous polarization of TTF-CA by first-principles calculations using our in-house computational code QMAS (Quantum MAterials Simulator), which is based on the projector augmented-wave (PAW) method with the planewave basis set. Calculations were made not only on the experimental structure \cite{1} but also on computationally optimized ones. The obtained electronic band structures are in good agreement with those reported by Oison \textit{et al.} \cite{2}. The spontaneous polarization for the experimental structure is estimated to be 0.10 C/m\(^2\), which is significantly larger than the experimental value of 0.4 x 10\(^{-2}\) C/m\(^2\) reported by Collet \cite{3}. We discuss the origin of the large spontaneous polarization from the present calculation as well as possible sources for the discrepancy between the calculation and the experiment.

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\begin{thebibliography}{9}
\bibitem{3} E. Collet, Ph.D thesis, University of Rennes 1, (1999).
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