Density Functional Theory Simulation of Iron-Montmorillonite as Carbon Dioxide Adsorber

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Abstract

Carbon dioxide (CO_2) is a greenhouse gas that naturally keeps the Earth's surface temperature warm, but currently the levels cause environmental problems such as climate change. Carbon capture and storage (CCS) technology is built to reduce CO_2 gas emissions by binding carbon dioxide molecules from sources and then storing them or utilizing them as more useful products. In this study, simulations were carried out for the addition of iron (Fe) impurities as an additional cation in montmorillonite to see the increase in the ability to bind carbon gas. Density Functional Theory calculations were carried out using additional corrections such as Van der Waals (vdW) and Hubbard-U. Here we got that Fe cation can help CO2 adsorption compared with other sites without Fe atom by adding acid cite condition. But to adsorb CO_2, the structure needed an initial process to swell the montmorillonite interlayer to a certain optimum distance.

Keywords: Adsorption, Carbon Capture, Interlayer, Montmorillonite.

INTRODUCTION

CO_2 is a greenhouse gas that plays a role in keeping the earth's surface warm by reflecting part of heat radiation. An increase in CO2 emissions to the atmosphere that is greater than the normal amount can raise the surface temperature of the Earth. The ultimate effect of this condition can be radical climate change that affects other environments, like melting polar ice and rising sea levels [1]. To anticipate this condition, carbon capture and storage (CCS) technology was developed. This research was focused on materials for capturing carbon from the environment. One material that can be chosen as a carbon capture agent is clay-based material. Clay minerals such as smectite and montmorillonite can easily expand the structure by adsorbing water molecules and trapping CO_2 molecules in the interlayer region [2].

Montmorillonite (Mmt) is one of the smectite-group clay minerals that can naturally adsorb carbon dioxide at the interlayer, and this property depends on the hydrogen and cation placed in it [3]. Mmt itself is an abundant, inexpensive, and versatile material that is widely used as a catalyst for chemical reactions [4, 5]. Mmt structure can also be changed with acid or metal by an ion-exchange reaction [6].

Metal doping is currently used to improve the properties of montmorillonite to capture carbon dioxide. Several metals used, such as cobalt (Co), iron (Fe), chromium (Cr), zinc (Zn), and aluminum (Al), can also affect the adsorption rate and selectivity of MMT [7–8]. Iron, as the most abundant element in the Earth [9], can be an interesting option to modify montmorillonite structure by ion-exchange

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procedure. A study compared iron with other metal ions to desorbed CO_2 from an amine solution and showed that iron-Mmt had better desorption ability due to its relatively high acid site value and porosity [7], but here the Fe-Mmt structure has not been modeled clearly. Other studies showed that the iron atom can be doped in montmorillonite [10] computed using DFT, but in this study, the Fe atom acts as a doped atom in Na-Mmt. Previous studies investigated the possibility of the Fe atom as a cation in MMT to adsorb CO_2, but there are parameters that need to be added to represent a more realistic case. In this study, continuing the previous one, some parameters were used to give van der Waals and d-orbital corrections of Fe-Mmt. Here, we also investigate the structure in the interlayer phase that represents the contribution of montmorillonite layers, not as a surface that only gives one layer contribution.

SIMULATION MODEL

The Fe-Montmorillonite (Fe-MMT) model used is based on a previous study [11], where there are two tetrahedral layers and one octahedral layer, with the addition of replacing two aluminum atoms with magnesium. The basic structure of MMT has a total of 40 atoms, consisting of 24 atoms of oxygen (O), 8 atoms of silicon (Si), 2 atoms of magnesium (Mg), 2 atoms of aluminum (Al), and 4 atoms of hydrogen (H). In this structure, there was no water molecule at the interlayer to represent the dry condition of Mmt. This condition is because moisture conditions reduce gas adsorption, where water molecules prevent CO_2 diffusion to Mmt pores [12].
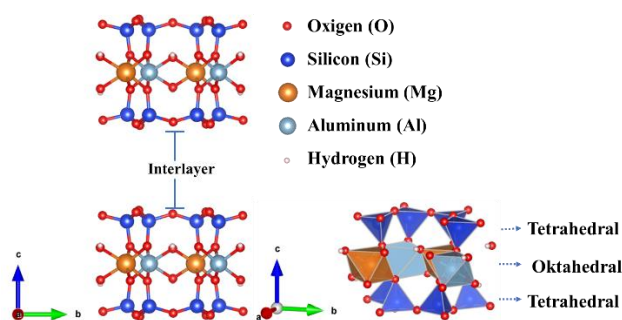

Figure 1. MMT structure model for interlayer distance optimization

From the montmorillonite structure, the optimum distance from the interlayer was scanned, which is the vacuum area of the design. Fe atoms are added as additions in the interlayer region at the optimum distance. Generally, the parameter lattice dimensions used are a = 5.276Å and b = 9.092Å, while the parameter c is varied to find the optimum interlayer distance.

In the optimum interlayer distance of Mmt, Fe atom was placed in the middle of the interlayer above the empty space between the tetrahedral parts. The CO_2 molecule is then introduced in the middle of the interlayer of Fe-Mmt relaxed structure for scanning the interlayer to get an optimized interlayer distance to adsorb CO_2. This procedure is also done for pure Mmt and some different cations as a comparison, such as Na, Ca, Li, and K. Here is also calculated the adsorption of CO as a comparison to CO_2 adsorption in Fe-Mmt.

CALCULATION METHOD

Calculations were carried out to observe the electronic properties using the Vienna Ab Initio Simulation Package (VASP) program based on the density functional theory (DFT) method [13, 14]. The exchange-correlation energy parameter uses the GGA approach with PBE functionality [15]. The simulation was carried out using a cut-off energy of 520 eV with a K-point of 5×5×1 based on the Monkhorst-Pack method [16]. In this calculation, the van der Waals (vdW) interaction developed by Grimme is introduced to give a correction for long-distance interaction. Other corrections are also used to give a better result for atoms that have *d*-orbitals with U and J values chosen for Fe of 4.00 and 0.00.

Some energy value described in this study represent Cation Binding Energy, Widening Energy and Adsorption energy that generally formulated below

$$E_{(Cat-binding)} = E_{(Cat-Mmt)} - [E_{(Mmt)} + E_{(Cat)}] \quad (1)$$

$$E_{(Widening)} = E_{(Cat-Mmt\prime)} - E_{(Cat-MMT)} \quad (2)$$

$$E_{(ads)} = E_{(adsorbate/adsorbent)} - [E_{(adsorbate)} + E_{(adsorbent)}] \quad (3)$$

where cation-binding energy explain the energy of Montmorillonite structure to bind the cation. Widening energy come from comparison of two similar structure with different interlayer distance that represent energy to make the interlayer larger. Adsorption energy simply said explain about energy that used to adsorb or catch adsorbate in adsorbent structure, such as CO_2 in iron montmorillonite.

RESULTS AND DISCUSSION

First, the scanning process to get the optimum interlayer of MMT results in the graph in Figure 2. This graph shows relative energy as a function of interlayer distance. Relative energy is defined as the difference between the total

energy of each interlayer and the total energy of the longest interlayer distance, so this energy describes the connection energy between each layer of Mmt. From figure 2, the optimum distance of Mmt is predicted at 3 Å, and by relaxing the structure, the optimum structure got 2.9 Å interlayer distance. At this optimum distance, the Fe atom is placed in the interlayer.
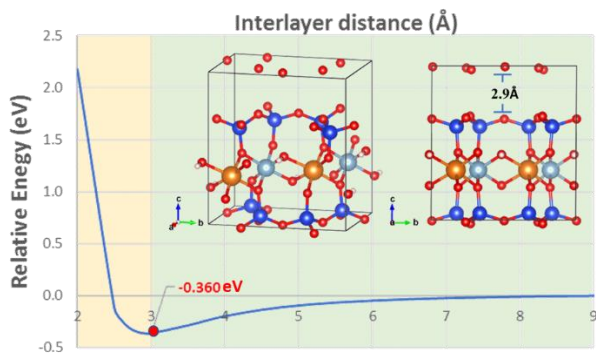

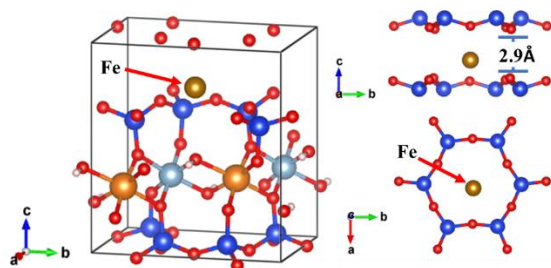**Figure 2**. Graph of scanning process to get optimum Mmt interlayer
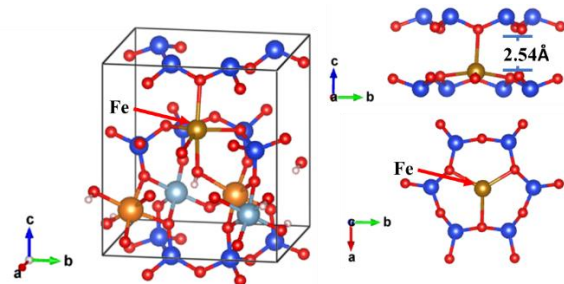

Figure 3. Initial position of Fe to get Fe-Mmt structure

Figure 4. Optimized structure of Fe-Mmt

To get adsorption information for CO_2 at the Fe-Mmt Interlayer, CO_2 molecule placed in the middle of interlayer in x-axis orientation. By manually scanning the interlayer, the optimum distance of interlayer to adsorb CO2 was obtained, as shown in Figure 5. At the optimum interlayer, comparing the total energy with the optimum Fe-Mmt (with 2.5Å interlayer), resulting positive adsorption energy value +0.477eV. Changing the point of view, using Fe-Mmt with 4.6 Å interlayer, gives negative energy

of -0.6613V. By comparing the Fe-Mmt structure of two interlayers without CO_2 as described using formula (2), resulting +1.138 eV showed energy to make the interlayer larger. This condition describes that for adsorbing CO_2, the interlayer needs to swell to a certain distance that comes from external aspect such as water molecule preadsorption.
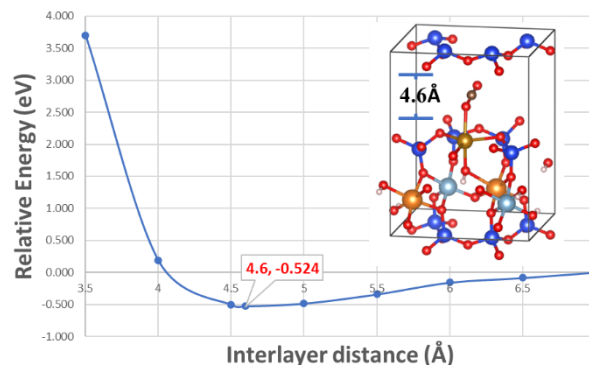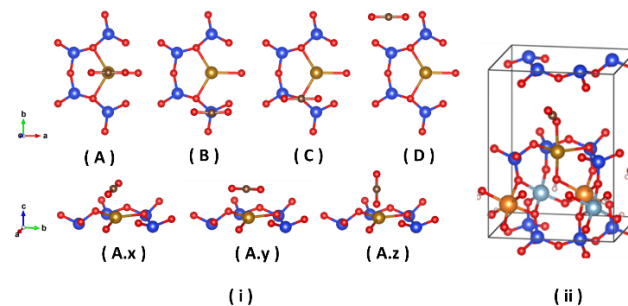

Figure 5. Optimized interlayer of Fe-Mmt to adsorp CO2

Figure 6. (i) Variate CO_2 molecule position and orientation. (ii) Optimum structure of CO2 adsorption to Fe-Mmt

Using the optimum structure to adsorb CO_2, variate position and orientation of CO_2 molecule introduce, as shown in Figure 6, to get the optimum position to adsorb CO_2. The result of these calculations is shown in Table 1. Here, several cases came from different initial introductions of CO_2. It is shown that the most spontaneous case that is possible is when CO_2 comes above the iron atom with *x*-orientation. The -0.806eV adsorption energy that was obtained means that the CO_2 molecule spontaneously adsorbs to Fe-Mmt and forms a bond with the iron atom. On the other side, when CO_2 came above the empty silicate place, the adsorption also happened with lower energy, which represents a physisorption condition come from vdW interaction, and the bonding did not appear.

Table 1. Result of CO_2 adsorption to Fe-Mmt at variate position and orientation

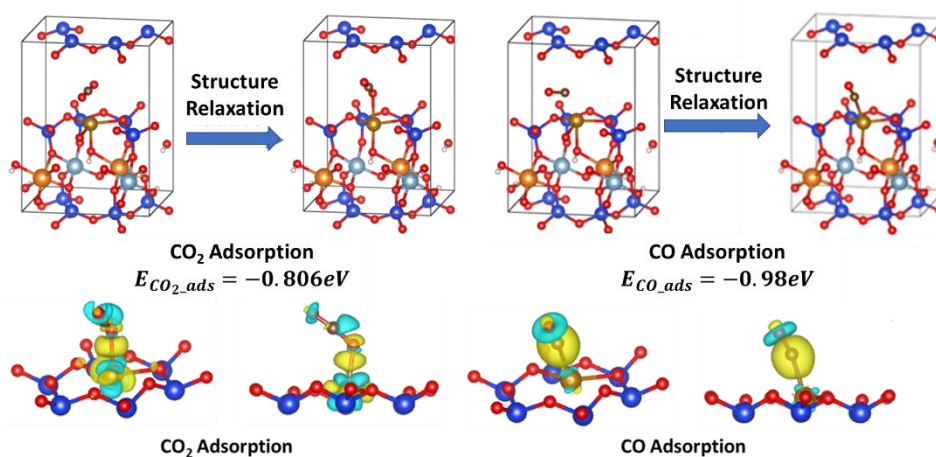| Structure	Orientation	E ads (eV)	Case
C atom above Fe atom	X	-0.806	Chemisorption
	Y	0.025	nonspontan
	Z	-0.783	Chemisorption
C atom above Si atom	X	0.125	nonspontan
	Y	-0.470	Chemisorption
	Z	-0.129	Physisorption
C atom above O atom	X	0.141	nonspontan
	Y	-0.382	Chemisorption
	Z	-0.365	Chemisorption
C atom above Silicate ring	X	-0.154	Physisorption
	Y	-0.122	Physisorption
	Z	0.137	nonspontan

As a comparison of this result, another different cation was processed to get the Fe-Mmt structure to adsorb CO_2. By varying the cation, the interlayer of Mmt becomes larger or shorter depending on the size of the atom. Just seeing the five cations problem, atoms with a smaller size than Na atom will shrink the interlayer, while potassium that have bigger size than Na can swell the interlayer. Table 2 shows the binding energy of each atom condition, and it can be said that for stronger binding energy, higher external

energy is needed to swell the interlayer to its optimum structure for adsorbing CO_2. For groups IA and IIA cations, the Ca atom as a cation has the highest value of adsorption energy. But compared with Fe, which has a similar pattern of shrinking and widening energy, the Fe atom results in stronger adsorption energy for CO2, which could be affected by d-orbital contribution that give better acid site.

Talking about the carbon capture system that is trying to adsorb CO_2, it made me curious: why is the carbon capture system not bonding to the C atom. Trying to answer this question, the calculation of the Fe-Mmt system to adsorb carbon monoxide (CO) molecules has been done and shown in Figure 7. I found that the Fe-Mmt structure can adsorb CO slightly easier than CO_2 with a 0.174 eV adsorption energy difference. It can be said that adsorbing CO has stronger adsorption when the Fe atom of Fe-Mmt forms a bond with the C atom. Further charge density analysis was done and showed that for the C-F bonding case, a high charge accumulated in the C atom that could come from an atom that lost

Table 2. Result of CO_2 adsorption to Fe-Mmt at variate position and orientation

Structure	Opt Interlayer (Å)	Binding Energy (eV)	Opt Int to adsorb CO2 (Å)	Widening Energy (eV)	CO_2 ads Energy (eV)
Mmt	2.9	-	4.0	0.166	-0.144
Fe-Mmt	2.5	-7.84	4.6	1.138	-0.806
Na-Mmt	2.9	-4.247	5	0.607	-0.422
Li-Mmt	2.8	-4.430	4.5	0.397	-0.491
Ca-Mmt	2.5	-8.536	4.5	1.139	-0.573
K-Mmt	3.4	-4.174	5.5	0.556	-0.290

CO2 Adsorption
$E_{CO_2\_ads} = -0.806 eV$

CO Adsorption
$E_{CO\_ads} = -0.98 eV$

CO2 Adsorption

CO Adsorption

Figure 7. Comparison of CO_2 and CO adsorption shown in atomic structure and charge density with yellow and blue region represent charge accumulation and depletion respectively
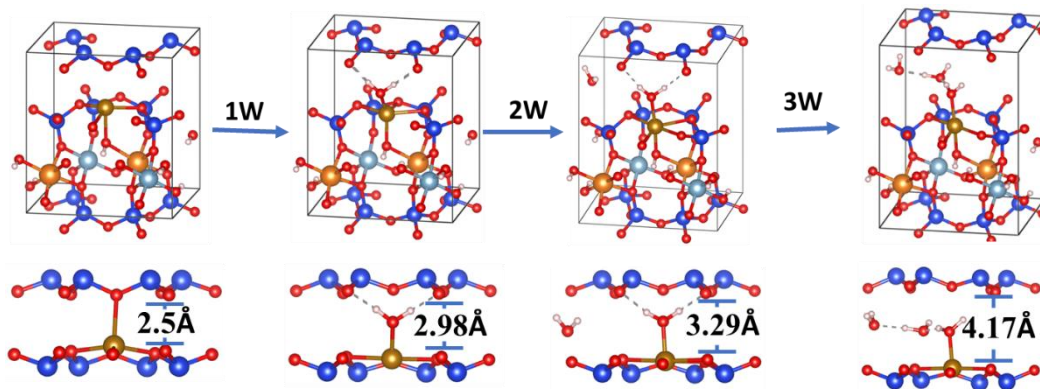
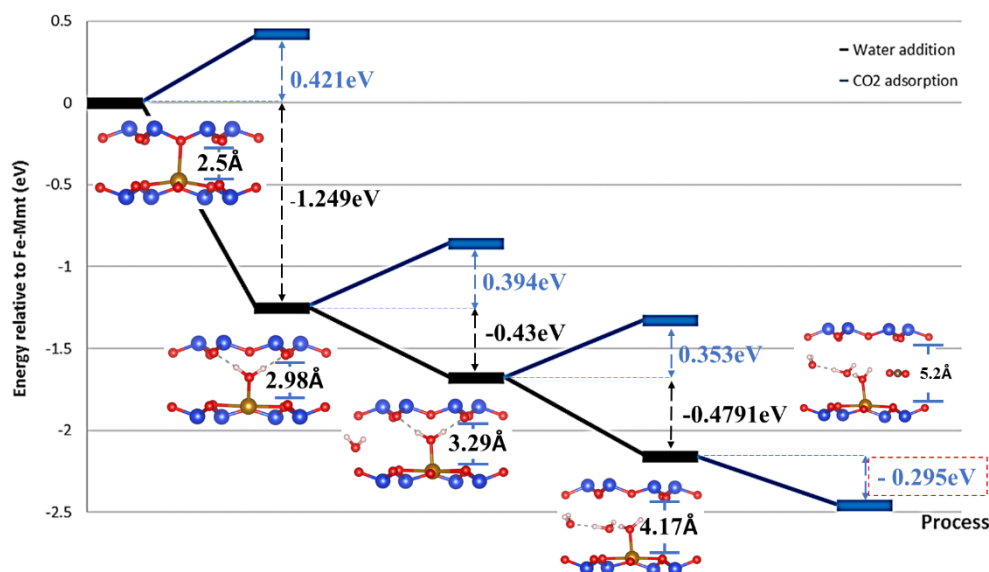**Figure 8.** Water molecule adsorption to swell the interlayer

Figure 9. Energy diagram of water molecule reaction to intelayer swelling

charge. Also, here it can be seen that charge in Fe atom did not significantly change, different with CO_2 case that the adsorption case centered in Fe atom.

Looking back, previous results mention that an external aspect needed to swell the interlayer; water molecules were gradually introduced to 2.5Å interlayered molecules. It is shown, as drawn in Figure 8, that for each water molecule addition, the interlayer of Fe-Mmt becomes larger little by little. At every step, CO_2 molecule was tried to be introduced into the interlayer, and the adsorption energy is summarized in Figure 9. It can be seen that for one and two water molecules, even though the interlayer became larger, it was not large enough to adsorp CO_2. With the addition of three water molecules, it can be said that the interlayer is already large enough to adsorb CO2, even though it was not the optimum interlayer as gotten in previous point. The resulted adsorption energy is not as strong

as what was mentioned before; it is only -0.295 eV and represents physisorption phenomena. Apart from the fact that the interlayer is not at the optimum distance, this condition also happened because the water molecules that help the swelling process took the place of the possibility of a Fe atom making a bond. But this condition still opens up the possibility for Fe-Mmt to adsorb CO2 in the interlayer.

CONCLUSION

Using the DFT method with vdW and *d*-orbital correction, Fe-Mmt was investigated as a CO_2 adsorbent. Fe-Mmt results in better adsorption energy than several group IA and IIA atoms but needs external energy higher to reach the optimum interlayer to adsorb CO_2. Confirming the carbon capture term, compared with CO bonding, Fe-Mmt can tie CO molecules slightly stronger than CO_2 caused by Fe-C

bonding for CO, which can be said to be stronger than Fe-O bonding for CO_2. To make the interlayer swell to a suitable distance, at least three water molecules are needed to adsorb in the interlayer of Fe-Mmt.

REFERENCES

[1] Topham, S., Bazzanella, A., Schiebahn, S., Luhr, S., Zhao, L., Otto, A., & Stolten, D. *Carbon Dioxide, In Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH Verlag GmbH & Co. KGaA., 1, 2014.

[2] Romanov, V. N., Ackman, T. E., Soong, Y. & Kleinman, R. L. CO 2storage in shallow underground and surface coal mines: Challenges and opportunities. *Environmental Science and Technology* **43,** 561, 2009.

[3] Romanov, V. N. Evidence of irreversible CO2 intercalation in montmorillonite. *International Journal of Greenhouse Gas Control* **14,** 220, 2013.

[4] Bhatti, U. H. *et al.* Practical and inexpensive acid activated montmorillonite catalysts for energy-efficient CO2 capture. *Green Chemistry* **22,** 6328, 2020.

[5] Nagendrappa, G. Organic synthesis using clay and clay-supported catalysts. *Applied Clay Science* **53,** 106, 2011.

[6] Bhatti, U. H. *et al*. Ion-exchanged montmorillonite as simple and effective catalysts for efficient CO2 capture. *Chemical Engineering Journal* **413,** 2021.

[7] Bhatti, U. H. *et al.* Facilely Synthesized M-Montmorillonite (M = Cr, Fe, and Co) as Efficient Catalysts for Enhancing CO2 Desorption from Amine Solution. *Industrial and Engineering Chemistry Research* **60,** 13318, 2021.

[8] Jha, A., Garade, A. C., Shirai, M. & Rode, C. V. Metal cation-exchanged montmorillonite clay as catalysts for hydroxyalkylation reaction. *Applied Clay Science* **74,** 141, 2013.

[9] Frey, P. A. & Reed, G. H. The ubiquity of iron. *ACS Chemical Biology* **7,** 1477, 2012.

[10] Ferreira, C. R. *et al*. Structural and Electronic Properties of Iron-Doped Sodium Montmorillonite Clays: A First-Principles DFT Study. *ACS Omega* **4,** 14369, 2019.

[11] Wungu, T. D. K *et al*. Adsorption of CO2 on Fe-montmorillonite: A density functional theory study.*AIP Conference Proceedings* **2384,** 2021.

[12] Khajeh, M. & Ghaemi, A. Nanoclay montmorillonite as an adsorbent for CO2 capture: Experimental and modeling. *Journal of the Chinese Chemical Society* **67,** 253, 2020.

[13] Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Physical Review B* **48,** 13115, 1993.

[14] Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B-Condensed Matter and Materials Physics* **54,** 11169, 1996.

[15] Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Physical Review Letters* **77,** 3865, 1996.

[16] Monkhorst, H. J., & Pack, J. D. Special points for Brillonin-zone integrations* Hendrik. *PHYSICAL REVIEE B* **13,** 5188, 1976.