Theory of the Verwey transition in Fe_3O_4

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Abstract

The metal-insulator transition in magnetite Fe_3O_4, the so-called Verwey transition, is re-investigated theoretically, motivated by recent experiments. We propose a scenario other than charge order, which has been considered to be its origin so far. We find that the orbital order in the t_{2g} orbitals can make the system effectively one-dimensional, so that the bond dimerization is induced due to the Peierls instability. Based on considerations of the elastic energy in the presence of such bond dimer, we argue that an anti-phase configuration of these bond dimer is realized in the actual compound.

Key words: magnetite ; metal-insulator transition ; charge order ; orbital order

1. Introduction

The metal-insulator phase transition in magnetite, Fe_3O_4, at 120 K ($=T_V$), has been attracting interest from its discovory in 1939 by Verwey [1]. Despite intensive studies since then to clarify its nature, the origin of this transition remains to be solved [2]. The most believed scenario has been the charge ordering, where the valence of the Fe ions changes at T_V. Since the valence of the one third of the Fe ions, occupying the A sites of the spinel structure, is unchanged as 3+ through the entire temperature range, the stage of this charge ordering is the remaining two third, that is the Fe ions at the B sites. It is argued that their valence of 2.5+ above T_V changes below T_V as 2+ and 3+ with 1:1 ratio. However, the actual pattern of this charge order has not been determined yet. Recently, several different papers have casted doubt on the existence of such charge ordering below T_V [3–5].

One possible reason why the charge order is not stablized is the geometrical frustration, as was pointed out by Anderson [6]. The Fe ions situated on the B sites form a pyrochlore stucture, known as a frustrated structure, where the charge order should be considerably suppressed. If it is suppressed completely, then another scenario is needed to explain the Verwey transition in magnetite, which we will present in this paper.

2. Model

The effective model for the Verwey transition at the Fe(B) sites we consider is the three-band spinless fermion model [8]. The three bands represent the t_{2g} orbitals under the crystal field due to the octahedral surrounding of oxygens. The spinless fermion picture originates from the fact that the spins are fully polarized for the B sites, which is due to the ferrimagnetic Neel ordering at 860 K between the Fe ions at the A sites and those at the B sites. Actually, the validity of such model is confirmed by band calculations [9]. We use the tight binding parameters determined by those band calculations, providing very anisotropic transfer integrals [9]. Note that the valence of 2.5+ of the Fe(B) ion corresponds to $(3d)^{5.5}$ occupancy, so that in the

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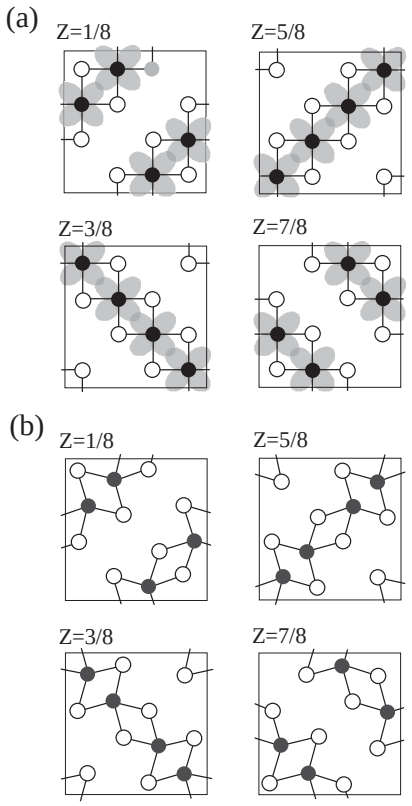

Fig. 1. Schematic views of the proposed (a) orbital order and (b) bond dimer in magnetite Fe_3O_4. The black and white circles represent the Fe and O ions, respectivley, and the gey area in (a) represent the xy orbital order. For details, see ref. [7]

high spin configuration the majority spin band is fully occupied and the minority band has 0.5 electron per site in the t_{2g} orbital, thus the model is 1/6-filled. Here, we also include the on-site Coulomb interaction as well as the lattice degrees of freedom by a Peierls type coupling [7], which play crucial roles as seen in the following.

3. Orbital Order and Bond Dimerization

Self-consistent mean field calculations [7] show that an orbital ordered state is stabilized below around 6000 K for realistic values for magnetite. This orbital order, as shown in Fig. 1 (a), is a ferro-type (say, xy orbital) order with arrays of Fe ions having effectively quasi one-dimensional electronic structure. This quasi one-dimensional state shows the Peierls instability with a period of two Fe sites, stabilized well below the orbital ordering phase transition temperature when we have moderate value of the electron-lattice coupling. This state is called as the bond dimerized state, which is insulating. We propose this bond dimerization to be the origin of the metal-insulator transition in magnetite Fe_3O_4.

As for the actual three-dimensional pattern of the bond dimers, we have constructed a semi-phenomenological model including the lattice elastic energy for all the neighboring Fe(B)-O bonds as well as Fe(A)-O bonds, which are important in determining the actual bond dimer pattern. The numerical results [7] shows that an anti-phase bond dimer pattern should be stabilized in magnetite, as shown in Fig. 1 (b). This state consistently explains many experimental facts, e.g., it reproduces the large unit cell size determined experimentally [2].

4. Summary

In summary, we have presented a new scenario for the metal-insulator transition in magnetite Fe_3O_4. The origin of the insulating state is the bond dimerization induced by the Peierls instability, which is the consequence of the ferro-type orbital ordering due to the strong Coulomb interaction.

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