Itinerant d electrons in spinels

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Abstract
We review a number of different approaches which have been used in order
to explain the physical properties of some metallic spinels, in particular of
magnetite Fe_3O_4 and LiV_2O_4. It is also pointed out that in geometrically
frustrated lattices such as the pyrochlore structure one may have excitations
with fractional charge.

1. Introduction

Spinels have the composition AB_2O_4 and can be considered as face centred cubes of O^{2-} ions.
The B ions are surrounded by an octahedron of O^{2-} ions, i.e., BO_6, and are positioned on
corner-sharing tetrahedra. The latter form a pyrochlore lattice. Often the pyrochlore lattice
is called a geometrically frustrated lattice. There exists a large amount of work dealing with
pyrochlore lattices with a spin, e.g., of $1/2$ attached to each lattice site. In the case of an
antiferromagnetic nearest neighbour interaction the ground state is believed to be a spin liquid
since the interactions are frustrated. A large fraction of the present conference is dealing with
various effects and physical phenomena based on those spin frustrations.

Here we are interested in a different type of situation. We want to review a number of
approaches which deal with metallic spinels in which the electrons are itinerant. There are three
spinels which belong into that category. They are Fe_3O_4 (magnetite) as well as LiV_2O_4 and
$LiTi_2O_4$. The three materials have quite different physical properties. A characteristic feature
of Fe_3O_4 is a metal–insulator transition at 120 K due to charge order. Quite different is LiV_2O_4.
Here it was found that the system has heavy quasiparticle excitations at low temperatures [1]. It
is considered the first case of a d-electron system found with heavy fermion behaviour, despite
the fact that $(YSc)Mn_2$ shows similar features [2, 3]. Finally, $LiTi_2O_4$ is a superconductor with
a relatively high transition temperature of $T_c = 13.7$ K [4, 5].

In the following we shall discuss a number of different approaches which were suggested
in order to explain the heavy quasiparticle behaviour of LiV_2O_4. Before doing this we want to
discuss briefly the case of Fe_3O_4 and what we learn from it. Towards the end we want to bring
to attention some thoughts about a possible appearance of excitations with fractional charges
in frustrated lattices like the pyrochlore or checkerboard one.

2. A reminder of Fe_3O_4

Magnetite Fe_3O_4 is one of the most studied minerals because of its important role in magnetism. It has the spinel structure AB_2O_4 with A = Fe^{3+} and B = $Fe^{2,5+}$. Because we may assume that the intra-atomic correlations on a Fe site are rather strong we may safely assume that 50% of the B sites are in a Fe^{2+} configuration and 50% are in a Fe^{3+} one, i.e., fluctuations into other configurations such as Fe^{1+} or Fe^{4+} etc are suppressed. Verwey and Haayman [6] observed around 120 K a phase transition from a high temperature metallic into a low temperature insulating phase. This transition is named after Verwey who presented a model for that transition. According to his model one is dealing here with an entropy driven order–disorder phase transition. The prerequisite is a sufficiently strong nearest neighbour interaction between the B sites Fe^{3+} and Fe^{2+}. Let us denote the interactions between two neighbours $Fe^{\alpha+}$–$Fe^{\beta+}$ by $V_{\alpha\beta}$ and neglect the delocalization of the d electrons, i.e., we treat them as being nearly localized. In that case an order–disorder transition may take place, provided that

$$\delta V = V_{33} + V_{22} - 2V_{23} > 0. \tag{1}$$

Verwey suggested a low temperature phase in which the Fe^{2+} and Fe^{3+} ions order along two families of chains in a pyrochlore lattice with one family pointing, e.g., in the (110) and the other in the [1–10] direction. But it was pointed out by Anderson [7] that in the presence of nearest neighbour interactions only, there are an exponentially large number of different states with the same repulsion energy as in Verwey's structure. This is a special feature of the pyrochlore lattice. All states in which the tetrahedra are occupied by two Fe^{3+} and two Fe^{2+} ions have the same repulsive energy (tetrahedron rule). Therefore in the absence of hopping or kinetic energy processes the ground state is highly degenerate. It is still an unsolved problem how this degeneracy is lifted by the inclusion of the kinetic energy terms, by longer ranged interactions or by lattice distortions. In any case, it is important to realize that a computation of the phase transition temperature must take into account that there are many distributions of the Fe^{2+} and Fe^{3+} ions possible with almost the same energy. Otherwise one would find a much too high transition temperature. For a conventional order–disorder phase transition the latter would be given by $T_V = 2\delta V/k_B$, where k_B is Boltzmann's constant, and of the order of several thousands of kelvins.

3. LiV_2O_4—some basic facts

As pointed out above, LiV_2O_4 is considered the first system found involving d electrons which shows heavy quasiparticle behaviour. The coefficient γ of the low temperature specific heat $C = \gamma T$ is enhanced and of order $\gamma \simeq 0.4$ J mol^{-1} K^{-2}. The spin susceptibility shows a behaviour

$$\chi_S = \chi_0 + \frac{c}{T + \Theta}, \qquad \Theta = 63 \text{ K} \tag{2}$$

which is Curie–Weiss-like at high temperatures. The susceptibility is equally enhanced at low T as is the coefficient γ. The Sommerfeld–Wilson ratio $R_W = \pi k_B^2 \chi_S(T = 0)/(3\mu_B^2 \gamma)$ is found to be of order unity. Furthermore, the resistivity is found to be $\rho(T) = \rho_0 + AT^2$ with a large coefficient $A = 2$ $\mu\Omega$ cm K^{-2}. These are typical hallmarks of heavy fermion systems. When the entropy $S(T)$ is calculated from the specific heat data one finds that $S(T = 60 \text{ K}) - S(T = 2 \text{ K}) = 10$ J mol^{-1} K^{-1} which is close to $2R \ln 2$ where R is the gas constant. This implies that at 60 K we must have almost one excitation per V ion. This is inconceivable with a conventional band description of the 3d electrons. A number of calculations based on the local density approximation (LDA) to density functional theory
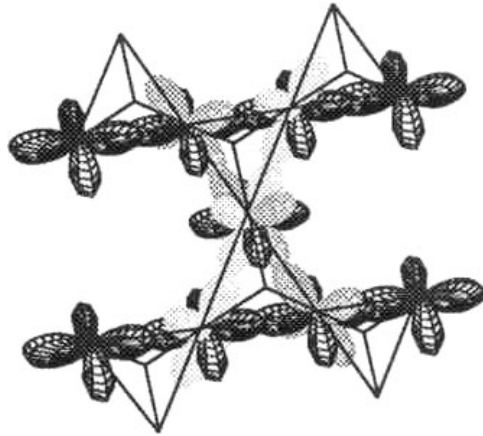
Figure 1. Decomposition of t_{2g} orbitals so that they form three 1D bands (from [10]).

show that the electrons around the Fermi energy are of 3d t_{2g} character. These states are well separated from the e_g states as well as from the oxygen p states. But the width of the t_{2g} bands is of order 2 eV and therefore at 60 K only a small fraction of those electrons can be excited due to Pauli's principle. In fact, a factor of 25 is missing in the calculated density of states for explaining the observed large γ value.

Finally, it is important to know that under hydrostatic pressure LiV_2O_4 undergoes a phase transition into an ordered state at approximately 6 GPa [8]. This indicates that nearest neighbour charge interactions are important in that material, like in Fe_3O_4. In the following we want to discuss a number of different theories which have been advanced to explain these experimental findings.

4. Weak coupling approaches

One suggestion which has been made to explain the heavy quasiparticles is based on multi-component fluctuations [9]. The fluctuations due to the t_{2g} and spin degrees of freedom are described by introducing 35 generators of the $SU(6)$ group and calculating with them the corresponding generalized susceptibilities, i.e., $\chi_{nn'}^{\alpha\beta}$. Here n, n' denote the four different sublattices of the pyrochlore structure and α, β label the different generators. This matrix has the dimension 144×144 but decomposes into spin singlet and triplet sectors, where each sector is represented by a charge–charge and longitudinal spin–spin susceptibility. Those susceptibilities are calculated within the RPA based on a multiband Hubbard Hamiltonian. It includes on-site interactions but neglects interactions between different sites. From the imaginary part of the dynamical susceptibilities the free energy is calculated and from it the specific heat. For large on-site repulsions, i.e., $U > U_c$, the RPA susceptibilities diverge, but for $U \geqslant 0.8U_c$ where U_c is the critical repulsion one finds γ values of the observed size. However, the Wilson ratio $R_W \simeq 0.1$ instead of $R_W \simeq 1$–2 because of the large contributions of orbital degrees of freedom to the γ value.

Another model theory considers the pyrochlore structure of the V ions as a network of Hubbard chains [10]. Three families of quarter-filled Hubbard chains are considered pointing along $(1, \pm 1, 0)$, $(1, 0, \pm 1)$ and $(0, 1, \pm 1)$ (see figure 1). For simplicity it is assumed that a hybridization between different chains takes place at the *same* site instead of between different sites and furthermore that it is weak. Due to the one-dimensional features, electron correlations

have strong effects, e.g., on the spin susceptibility $\chi_S^{1D}(q, \omega)$. In fact, the latter diverges at a reciprocal lattice vector $q = Q_0$, but the singularity is removed when a crossover from 1D to 3D at a temperature T^* is taken into account. For $T > T^*$ the system behaves one-dimensionally, but for $T < T^*$ it is a three-dimensional Fermi liquid. When the self-energy $\Sigma(\omega)$ is calculated from $\chi_S^{1D}(q, \omega)$ with the smoothed singularity we can calculate from it

$$\gamma = \left(1 - \frac{\partial \Sigma}{\partial \omega}\bigg|_{\omega=0}\right)\frac{2\pi}{3v_F}, \tag{3}$$

and find values of the order of the observed size. The theory is applicable for T sufficiently close to T^*.

5. Theories with on-site d–d repulsions

There are a number of theoretical approaches which take a strong on-site Hubbard U at the V sites into account but neglect intersite interactions. Several of them keep one of the t_{2g} electrons as localized and consider the remaining 0.5 d electron per V site as itinerant. The following argument is used to justify this division. Due to a slight distortion of the oxygen octahedra surrounding the V ions the t_{2g} states of an ion split into an a_{1g} and two e'_g states. This splitting is small against the corresponding bandwidths. Also it is found within LDA [11–13] that the occupancies are $n(e'_g) = 1.1$ and $n(a_{1g}) = 0.4$. But when instead a LDA + U calculation is done the state with the lower orbital energy, i.e., the a_{1g} state, becomes singly occupied while the remaining 0.5 d electron is of e'_g character [14]. However, this seems to be a mean-field result and from an atomic point of view it is difficult to see why only one of the two d electrons of V^{3+} should be able to hop. In any case, when one d electron is considered as being localized one might ask about a possible Kondo effect occurring in LiV_2O_4. Of course, the on-site spin–spin interaction between a localized a_{1g} and an itinerant e'_g electron is ferromagnetic and of order $J_H \simeq 1$ eV due to Hund's rule coupling. The interaction between an a_{1g} electron and e'_g electrons of neighbouring sites is antiferromagnetic via V–O superexchange but small. There is also another ferromagnetic interaction contribution from double exchange. From these considerations it seems unlikely that a Kondo effect is operative in LiV_2O_4. Despite this it is an interesting problem to study the Kondo effect in a frustrated lattice [15]. The corresponding Hamiltonian is

$$H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \tilde{J} \sum_i S_i \sigma_i + \sum_{\langle ij \rangle} J_{ij} S_i S_j \tag{4}$$

where $\tilde{J} > 0$. The usual competition between the energy gain via the Kondo effect and the RKKY interaction is modified here, because there is no antiferromagnetic long range order possible in a frustrated lattice system. The effect of frustration can be taken into account by choosing for J_{ij} random variables with a variance $J/\sqrt{z}$ where z is the coordination number. When the limit of infinite dimensions $D \to \infty$ is considered the problem can be solved analytically within dynamical mean-field theory (DMFT) and the large N approach. At $T = 0$ there exists a critical coupling constant J_c which separates a spin liquid state $(J > J_c)$ from a heavy fermion regime $(J < J_c)$. In the limit of small J one finds essentially free spins at temperatures $T > T_K$ $(\simeq J_c/k_B)$ while below a coherence temperature $T^* < T_K$ one finds again a heavy Fermi liquid. At high temperatures where $k_B T \simeq J$ the spins turn from nearly free into a spin liquid.

In the following we discuss models which are based on equation (4) but with $\tilde{J} < 0$, i.e., with Hund's rule coupling. One way of taking the spin liquid in a pyrochlore structure into account is by assuming a nearest neighbour spin correlation of the form

$$\langle S_i S_j \rangle = -\tfrac{3}{2}\Gamma^2. \tag{5}$$

Similarly Hund's rule coupling can be treated in a mean-field approximation by requiring

$$\langle \boldsymbol{S}_i \boldsymbol{\sigma}_j \rangle = u^2. \tag{6}$$

The mean field is determined from a pseudo-hybridization between the a_{1g} electron described by the creation operator $a_{i\sigma}^+$ and the itinerant e_g' electrons with creation operators $c_{i\sigma}^+$:

$$\tilde{J} \sum_i \boldsymbol{S}_i \boldsymbol{\sigma}_i \rightarrow \tilde{J} u \sum_i (a_{i\uparrow}^+ c_{i\downarrow} + a_{i\downarrow}^+ c_{i\uparrow} + \text{h.c.}) + \frac{\tilde{J}}{2} u^2 N. \tag{7}$$

Here N is the number of sites and the subsidiary condition $\sum_\sigma \langle a_{i\sigma}^+ a_{i\sigma} \rangle = 1$ must be obeyed. There are two different temperatures of relevance. Above $T = T_{\text{mag}}$ the variable $\Gamma = 0$ and spin correlations are absent. In that regime a Curie–Weiss law holds. A vanishing mean field u marks the temperature T_{HF} ($\simeq 20$ K) below which we have a narrow a_{1g} band at E_F and therefore heavy quasiparticles [16].

The mean-field approach can be generalized by also treating the a_{1g} electron as itinerant and taking the on-site Coulomb repulsion between the a_{1g} and e_g' electrons in a slave boson mean-field approximation into account [17]. Similarly to in the LDA + U one obtains again a singly occupied a_{1g} orbital at each site. The two-band Hamiltonian is in this case

$$H = H_0(e_g, a_{1g}) + \sum_i H_w(i) \tag{8}$$

where the first term is the kinetic energy of the a_{1g} and e_g (described by one orbital only) electrons while $H_w(i)$ is the interaction part

$$H_w(i) = U(n_{e\uparrow}(i)n_{e\downarrow}(i) + n_{a\uparrow}(i)n_{a\downarrow}(i)) + U'n_e(i)n_a(i) + \tilde{J}\boldsymbol{\sigma}_e(i)\boldsymbol{\sigma}_a(i) \tag{9}$$

with $\tilde{J} < 0$. The subscripts e and a refer to e_g' and a_{1g} orbitals, respectively. It is assumed that the orbital energy of the e_g' electrons is 0.2 eV higher than that of the a_{1g} orbital. Furthermore, $U \rightarrow \infty$ is assumed and $U' \simeq 3$ eV and $\tilde{J} \simeq -1$ eV. Five slave boson fields are introduced, i.e., for an empty site, a singly occupied one with an e_g' or a_{1g} electron and a doubly occupied site with a total spin $S = 0$ and 1. The corresponding mean-field values are e, p_e, p_a, $d_{S=0}$ and $d_{S=1}$. When the mean-field equations are solved for the parameter values described above it is found that $\langle n_a(i) \rangle \simeq 1$ because of the lower orbital energy. The corresponding a_{1g} bandwidth is strongly renormalized by a factor

$$q_a \simeq \frac{1 - \langle n_a \rangle}{1 - \langle n_a \rangle / 2} \ll 1 \tag{10}$$

as in the Gutzwiller approximation to the Hubbard model [18]. This gives rise to a sharp resonance at E_F and therefore to heavy quasiparticles.

Finally we discuss a model which goes beyond the mean-field approximation [19]. Again, it assumes that an a_{1g} electron is localized but it treats both e_g' orbitals labelled 1 and 2 so the Hamiltonian is

$$H = -\sum_{\langle ij \rangle} t_{12}(c_{i1\sigma}^+ c_{j2\sigma} + \text{h.c.}) + U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + U' \sum_i n_{i1} n_{i2}$$
$$+ \tilde{J} \sum_i \boldsymbol{S}_i (\boldsymbol{\sigma}_{i1} + \boldsymbol{\sigma}_{i2}) + J \sum_{\langle ij \rangle} \boldsymbol{S}_i \boldsymbol{S}_j. \tag{11}$$

The $\langle ij \rangle$ are nearest neighbour pairs and $\tilde{J} < 0$. Note the similarly with equations (4), (5). A strong ferromagnetic coupling between the a_{1g} and e_g' electrons is assumed by setting

$-\tilde{J} \to \infty$ and the spin correlations of the localized a_{1g} electrons imply that the hopping matrix element t_{12} changes to

$$t_{12}(S) = t_{12}\sqrt{1 + \langle S_i S_j \rangle / 2S^2} \tag{12}$$

like in the manganites. The treatment of the spin correlations $\langle S_i S_j \rangle$ takes frustrations on the pyrochlore lattice into account [20]. When the limit $U \to \infty$ is taken the Hamiltonian simplifies to

$$H = -\sum_{\langle ij \rangle} t_{12}(S)(c_{i1}^+ c_{j2} + c_{i2}^+ c_{j1} + \text{h.c.}) + U' \sum_i n_{i1} n_{i2}. \tag{13}$$

That is, for the c_i operators there remains only one additional index. The latter plays the role of a pseudospin. Therefore H has the form of a Hubbard Hamiltonian which is treated by iterated perturbation theory close to quarter-filling. With increasing U' a Kondo-like sharp resonance is obtained resulting in heavy quasiparticles at low temperatures. The thermodynamics as well as the transport properties can be expressed in terms of a crossover temperature T^*, going from a heavy Fermi liquid to a spin liquid.

6. Model with nearest neighbour interactions

As pointed out before, LiV_2O_4 charge orders under pressure. This suggests that nearest neighbour interactions must be important. Therefore the following Hamiltonian should serve for a description:

$$H = -\sum_{\langle ij \rangle \nu} t_\nu (c_{i\nu\sigma}^+ c_{j\nu\sigma} + \text{h.c.}) + U \sum_{i\nu} n_{i\nu\uparrow} n_{i\nu\downarrow} + U \sum_{ij, \nu > \mu} n_{i\nu} n_{i\mu}$$

$$+ V \sum_{\langle ij \rangle} n_i n_j + \tilde{J} \sum_{i\nu\mu} s_{i\nu} s_{i\mu} + \sum_{\langle ij \rangle} J_{ij}(S_i, S_j) S_i S_j. \tag{14}$$

The notation is similar to before with $\nu = 1, 2, 3$ denoting the different t_{2g} orbitals. The important new term is the one including V and the charges $n_i = \sum_{\nu\sigma} n_{i\nu\sigma}$ at nearest neighbour sites i and j. One may safely assume that U is sufficiently large that only the configurations d^1 and d^2 are allowed and furthermore also that $\tilde{J}$ is large enough as compared with t_ν that the d^2 configurations have $S = 1$. The interactions J_{ij} will depend on the respective spins $S = 1/2$ or 1 at sites i and j.

Recalling that LDA band structure calculations require an additional effective mass enhancement by a factor of 25 in order to explain the low temperature specific heat, one may ask the question of whether the strong correlation limit would not make a better starting point [21]. In that case one has to neglect the kinetic energy term in equation (4) and take the hopping of electrons into account only via the effects on the spin interactions $J_{ij}(S_{ij} S_j)$. When the t_ν are neglected the tetrahedron rule must be obeyed. This implies that on each tetrahedron two sites are in a d^1 configuration with $S = 1/2$ and two are in a d^2 configuration with $S = 1$. There exist an exponentially large number of states which fulfil the tetrahedron rule. Each of these states consists of chains and rings of sites with $S = 1/2$ which are separated by chains and rings of sites with spin 1 [21]. This is a consequence of the pyrochlore structure. With the help of constrained LDA + U calculations one can determine the nearest neighbour coupling constants $J_{ij}(S_i, S_j)$. One finds values for $J(1/2, 1/2) = 3$ meV and $J(1, 1) = 24$ meV; i.e., spin 1 sites are much more strongly coupled to each other than spin 1/2 sites. In addition spin 1 chains or rings have a gap in the excitation spectrum (Haldane gap). Therefore the spin 1/2 chains and rings are virtually uncoupled from each other. The only way of coupling them
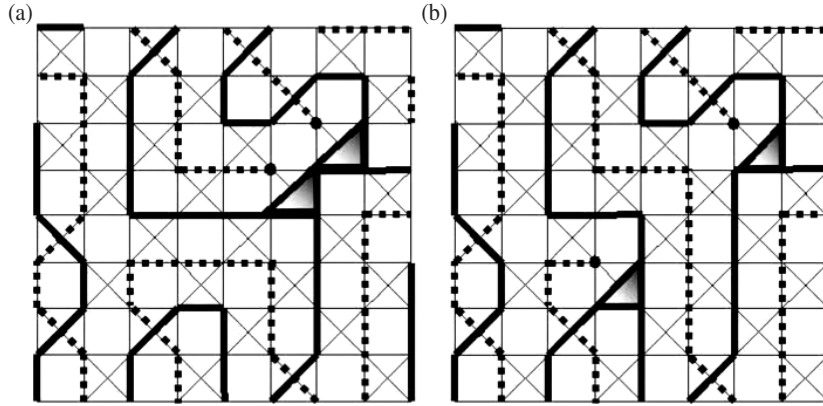
Figure 2. The checkerboard lattice consisting of an equal number of d^0 and d^1 configurations which are connected by dashed and solid lines, respectively. (a) One electron has been added so that the tetrahedron rule is violated on two tetrahedra (squares) marked as dark. (b) By a hop of an electron from the lower left corner the excitation has fallen apart into two pieces each with the charge $e/2$ (from [23]).

is via the spin 1 chains and rings and this coupling is in addition frustrated. Therefore one can determine the specific heat and susceptibility directly from [22]

$$\gamma = \frac{2}{3} \frac{k_{\mathrm{B}} R}{J(1/2, 1/2)}, \qquad \chi_S = \frac{4\mu_{\mathrm{eff}}^2 R}{\pi^2 J(1/2, 1/2)}. \tag{15}$$

Note that the Sommerfeld–Wilson ratio is $R_{\mathrm{W}} = 2$.

In order to explain the measured specific heat coefficient γ_{exp} one would need $J(1/2, 1/2) = 1.2$ meV, instead of the calculated 3 meV. It is known that LDA+U calculations overestimate spin interactions. In any case, the improvement which is needed here is much less than the factor of 25 when a band structure calculation is used as a starting point. The above considerations suggest that for LiV$_2$O$_4$ a frozen charge state is a much better starting point than a band structure calculation, at least as far as the low temperature thermodynamic specific heat and susceptibility are concerned. The latter are obviously robust with respect to the kinetic energy term. Why LiTi$_2$O$_4$ is so different from LiV$_2$O$_4$ remains an open question within that approach.

7. Fractional charge excitations in a pyrochlore lattice

It is interesting to realize that in a geometrically frustrated lattice such as a pyrochlore structure one can have excitations with fractional charge when electron correlations are strong. We demonstrate this by considering for better visualization a checkerboard structure instead. Furthermore, we assume an average of 0.5 electrons per site. We begin with a reduced Hamiltonian for spinless fermions of the form

$$H_{\mathrm{red}} = -t \sum_{\langle ij \rangle} \{f_i^+ f_j + \mathrm{h.c.}\} + V \sum_{\langle ij \rangle} n_i n_j. \tag{16}$$

Here f_i^+ (f_i) creates (destroys) a spinless fermion at site i and $n_i = f_i^+ f_i$. Assume that t/V is very small and that an electron is added to any of the configurations which obey the tetrahedron rule. In that case the rule is violated in two neighbouring tetrahedra, because of corner sharing. When the hopping is turned on, these two tetrahedra can separate from each

other without increase in the nearest neighbour repulsions (see figure 2). There is seemingly no restoring force in this model. Each of the two separate parts of the original excitation must have a charge $e/2$. When the spin is added to the considerations one finds that it is represented by a spin $1/2$ chain consisting of an *odd* number of sites. This chain connects the two tetrahedra which violate the tetrahedron rule and has a twofold-degenerate ground state. It represents the spin which here is distributed over large parts of the system. A finite kinetic energy will also generate vacuum fluctuations. Thereby an electron is hopping to a neighbouring empty site. As a consequence one of the tetrahedra contains one empty and three occupied sites (charge $e/2$) and another one has three empty sites and one occupied one (charge $-e/2$). There can be recombinations taking place between a charge $e/2$ from a vacuum excitation and that from an added electron. Therefore we expect a certain fraction of excitations with charge $e/2$ as well as with charge e. For further details we refer the reader to the original literature [23]. Excitations with fractional charges can also appear in other frustrated lattice systems.

Acknowledgment

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