Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetism in Two-Band Systems with Electron Correlation

Koichi Kusakabe [a] & Hideo Aoki [a b]

[a] Department of Physics, University of Tokyo, Hongo, Tokyo, 113, Japan

[b] Cavendish Laboratory, University of Cambridge, Cambridge, CB3 OHE, U.K.

Version of record first published: 05 Dec 2006.

To cite this article: Koichi Kusakabe & Hideo Aoki (1993): Magnetism in Two-Band Systems with Electron Correlation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 233:1, 71-80

To link to this article: http://dx.doi.org/10.1080/10587259308054948

Mol. Cryst. Liq. Cryst. 1993, Vol. 233, pp. 71–80
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MAGNETISM IN TWO-BAND SYSTEMS WITH ELECTRON CORRELATION

KOICHI KUSAKABE* and HIDEO AOKI*†

* Department of Physics, University of Tokyo, Hongo, Tokyo 113, Japan
† Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, U.K.

Abstract Magnetic phase diagram for the two-band Hubbard model in one dimension is explored. In the parameter space of direct and exchange interactions, the insulating ferromagnetism with an orbital superstructure transforms into metallic ferromagnetism as the strength of Hund's coupling is increased. When the orbital degeneracy is lifted, the ferromagnetic state is destabilized except in the region where metallic ferromagnetism appears.

INTRODUCTION

Although the origin of ferromagnetism is a long-standing problem indeed, it has yet to be fully understood. In considering the effect of strong electron correlation, the intra-atomic exchange interaction has been reemphasized as one of the most important factors since an early suggestion by Van Vleck.[1] His original idea to explain magnetism of $3d$-transition metals was followed by many investigations which concluded that the inter-atomic ferromagnetic exchange interaction causes the ferromagnetic ground state in the strong coupling limit.[2–7] In these studies, the two-band Hubbard model was intensively studied. The important consequence is that the fully polarized ferromagnetism accompanied by an orbital superstructure appears when there is one electron per atom on average with the band being 'quarter-filled'.

On the other hand, the mechanism of ferromagnetism based on the charge transfer interaction between molecules has been independently developed. Since an early suggestion by McConnell,[8] many ideas were proposed attempting to realize an organic ferromagnet.[9–12] Here, too, the orbital degeneracy in molecules plays an important role. Namely, a charge-transferred state prefers to take a spin-triplet configuration due to Hund's coupling. In fact, many authors concluded that in certain molecules the intra-molecular exchange interaction is strong enough to produce the

charge-transfer (CT) type inter-molecular ferromagnetic coupling.[13–15] Then, if the pairs of molecules are stacked into a column, the system will be ferromagnetic.

The situation is very similar to that considered for ferromagnetism in metals with degenerate bands. Indeed, Torrance et. al. have suggested a direct relation between the CT mechanism and the two-band Hubbard model. They considered a stack of radical anions for which a dianion has a triplet ground state due to the orbital degeneracy. This model can be described by the one-dimensional two-band Hubbard model.

If we employ the Hubbard model as a model of real organic materials, it is necessary to explore magnetism in finite-coupling region rather than the infinite coupling limit. Although the finite-coupling region has been studied with the mean-field approach,[5,6] the method may be unreliable when the electron correlations are strong. The numerical method for finite systems is exact and more appealing. For instance Gill and Scalapino have numerically obtained the magnetic phase diagram for a 4-site system in periodic boundary condition.[16,17]

The purpose of the present paper is :

(i) to look into what type of ferromagnetism appears as we change not only the interaction strength but also the size and the boundary condition of the system.

(ii) to examine the stability of the ferromagnetic state against the level offset.

In order to investigate the first point, we have numerically diagonalized the Hamiltonian for 4-site and 6-site systems in three boundary conditions, i.e., periodic, anti-periodic, and open ones. By this way, we can show that two different types of ferromagnetism appear in the parameter space of direct and exchange interactions. One is the conventional ferromagnetism with an orbital superstructure, where one of two orbitals in each site is occupied alternately along the chain. Here we stress that, even in this case, the strength of Hund's coupling must be comparable to the direct inter-orbital repulsion. This is because there are a greater number of spin-singlet exchange processes than triplet ones. Kollmar and Kahn[18,19] have in fact demonstrated that the singlet state of the donor-acceptor system gains much stabilization from many intermediate states which could invalidate McConnel's idea. Thus, a fairly strong intra-molecular exchange interaction is required for the ferromagnetic CT interaction.

The second and novel ferromagnetism has metallic properties which appears in

a region with larger intra-molecular exchange interactions. The mechanism of this ferromagnetism seems to have similarity with the strong-coupling limit of the two-band Hubbard model solved exactly by Kubo.[20] We shall show that metallic ferromagnetism obtained here may be accompanied by spiral spin states.

If one wishes to relate the degenerate Hubbard model to real materials, one should also look into the stability of ferromagnetism against the energy difference of two orbitals, Δ, that lifts the orbital degeneracy. It will be shown that ferromagnetism arising from the CT interaction is indeed destabilized by introducing Δ, whereas metallic ferromagnetism is fairly stable even when the level offset becomes as large as the transfer integral.

THE TWO-BAND HUBBARD MODEL

We employ the two-band Hubbard model in one dimension given by the Hamiltonian,

$$\begin{aligned} H &= -\sum_{i=1}^{N}\sum_{m,m',\sigma} t_{i,i+1}^{m,m'}(C_{i,m,\sigma}^{\dagger}C_{i+1,m',\sigma} + h.c.) + \frac{\Delta}{2}\sum_{i,\sigma}(n_{i,A,\sigma} - n_{i,B,\sigma}) \\ &+ U\sum_{i,m} n_{i,m,\uparrow}n_{i,m,\downarrow} + U'\sum_{i,\sigma,\sigma'} n_{i,A,\sigma}n_{i,B,\sigma'} - J\sum_{i,\sigma} n_{i,A,\sigma}n_{i,B,\sigma} \\ &- J\sum_{i}(C_{i,A,\uparrow}^{\dagger}C_{i,A,\downarrow}C_{i,B,\downarrow}^{\dagger}C_{i,B,\uparrow} + h.c.) \\ &- J'\sum_{i}(C_{i,A,\uparrow}^{\dagger}C_{i,A,\downarrow}^{\dagger}C_{i,B,\uparrow}C_{i,B,\downarrow} + h.c.), \end{aligned} \tag{1}$$

where $C_{i,m,\sigma}^{\dagger}$, $C_{i,m,\sigma}$ and $n_{i,m,\sigma}$ are the creation, annihilation and number operators, respectively, for an electron at the site i, in the orbital m $(= A, B)$ with spin σ. The number of the sites and the number of electrons are denoted by N and N_e, respectively. We identify $(N+1)$-th site as the first site when the periodic or the anti-periodic boundary condition is adopted. In this work, we assume the following transfer integrals, $t_{i,i+1}^{m,m'}$, for simplicity:

(i) The electron transfer exists only between nearest-neighbour sites.

(ii) The inter-orbital mixing, $t_{i,i+1}^{A,B}$, is ignored.

(iii) For both orbitals the transfer integral takes the same value with $t_{i,i+1}^{m,m} = t$.

As pointed out by Roth[2] the mixing term may be important in discussing the stability of ferromagnetism, but we adopt these assumptions to make the physical picture clear. The second term in the Hamiltonian represents the single particle energy difference, Δ, between the two orbitals.

The interactions, U, U' and J, represent intra-orbital repulsion, inter-orbital

repulsion and on-site exchange interaction, respectively. The last term in Eq.(1), sometimes neglected, is another exchange interaction whose magnitude should be of the same order as Hund's coupling. In the next section, the energy is calculated as a function of U' and J, while other parameters are fixed at $U = U' + J$ and $J' = J$ for simplicity. We take $t = 1$ as a unit of energy.

The energy eigenvalues are obtained for each spin state by Lanczos method. This is accomplished by taking an initial vector in the Lanczos iteration as an eigenfunction of the total spin. In order to characterize the wavefunction, we have calculated the spin-spin and density-density correlation functions from the wavefunction.

MAGNETIC PHASE DIAGRAM

General features

We can identify ferromagnetic phases at the absolute zero temperature by the energy difference, $E_{\text{ferro}} - E_{\text{singlet}}$, between the lowest ferromagnetic state and the lowest spin-unpolarized state. Spin-partially-polarized ground states have turned out to appear only in the vicinity of the phase boundary.

The result for the quarter-filled band ($N_e = N$) with $U = U' + J$, $J' = J$ and $\Delta = 0$ is shown in Figure 1. The phase diagram is obtained for both the periodic (PBC) and anti-periodic (APBC) boundary conditions. For the 4-site system with PBC the result for the ferromagnetic region agrees approximately with the result obtained by Gill and Scalapino, although they have neglected J'. We note here that, for both 4- and 6-site systems the ferromagnetic phase appears in a restricted region confined along the line $J = U'$. This means for instance that there is a critical value of $J_c \sim U'$ below which ferromagnetism is destroyed. The position of the phase boundary is seen to be sensitive not only to the system size, but also to the boundary condition. The latter feature indicates that the ferromagnetic wavefunction has an extended, metallic property, at least in the region where the appearance of ferromagnetism depends on the boundary condition.

Boundary for the ferromagnetism with the orbital superstructure

The ferromagnetism with orbital superlattice structures (OSL) as derived from the strong-coupling theory should not depend on the sign of t at the boundary because the effective Hamiltonian only contains the square of the transfer integrals. Thus the region for OSL ferromagnetism should be contained within the region where both

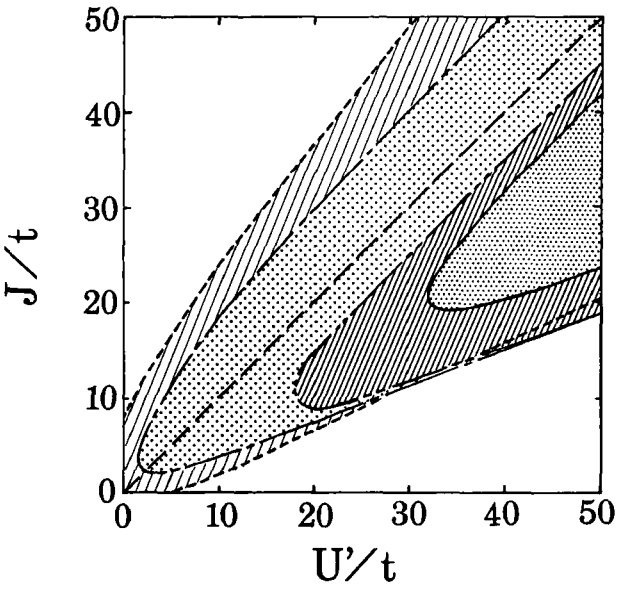

FIGURE 1 The magnetic phase diagram of the one-dimensional two-band Hubbard model against U' and J with $U = U' + J$, $J' = J$ and $\Delta = 0$ for the quarter-filling (one electron per site). Inner (outer) dotted area corresponds to the ferromagnetic phase in the 4-site (6-site) system with PBC, while outer (inner) hatched area represents that for the 4-site (6-site) system with APBC.

of PBC and APBC give ferromagnetism in Figure 1. The result for the correlation functions confirms that the ground state exhibits the staggered orbital ordering together with the inter-orbital ferromagnetic spin-spin correlation at the nearest-neighbour distance. Thus the picture given by the strong-coupling limit seems to hold in this region.

An analytic estimation of the lower boundary of the ferromagnetic region may be given by equating the antiferromagnetic exchange, $4Ut^2/(U^2 - J'^2)$, and the ferromagnetic exchange, $2t^2/(U' - J)$, between inter-orbital triplet configurations. Here the difference in the numerical factors between the antiferromagnetic and ferromagnetic exchange reflects the different numbers of possible exchange processes. Then we have the lower boundary as $J = U' - U/2 + J'^2/2U$, which is of the order of U' when $U \sim U'$. This is the reason why fairly large J, comparable to the direct repulsion, is required for ferromagnetism. More precisely, when we have $U = U' + J$ and $J' = J$, we end up with a quadratic equation for J yielding $J_c = (\sqrt{3} - 1)U'/2$, which approximately coincides with the lower boundary of the ferromagnetic region in Figure 1.

Novel metallic ferromagnetism in the two-band system

The mechanism of OSL ferromagnetism breaks down when J increases so that $U' - J \simeq \alpha t$ where α is of order unity. Above this upper boundary the system exhibits another ferromagnetism. For the 6-site system with PBC and the 4-site system with APBC, the ferromagnetic region extends well over the line, $J = U'$. The energy difference, $|E_{\rm f} - E_{\rm s}|$, becomes maximum ($\sim t$) around the line, $J = U'$.

We propose an intuitive picture for the spin-polarization mechanism working here. When J equals U', the net interaction between the two electrons with parallel spins in different orbitals becomes zero so that they can move freely, while they experience a large energy, $U' + J$, when they come to the same site if they form an inter-orbital spin singlet. Thus, in the strong coupling limit, the $S_{tot} = 0$ state consisting of inter-orbital singlets has excess nodes, which will increase the kinetic energy. This situation is similar to the mechanism proposed by Kubo in the strong-coupling limit, where the excess electrons beyond the quarter filling make the system metallic. In both cases, the restriction in the available phase space due to the large Hund's coupling is essential. We can show that the ferromagnetic ground state appearing near $J = U'$ line is the direct product of the Nagaoka-Stoner Fermi sea for the band A and that for the band B. Both of two Fermi seas are filled with electrons whose spins are aligned in the same direction. Here all the states at the Fermi level are occupied for the 6-site system with PBC and the 4-site system with APBC.

The singlet ground states for the 4-site system with PBC and the 6-site system with APBC on the line $J = U'$ have a spiral spin structure (Figure 2). This is reminiscent of metallic ferromagnetism in the Nagaoka state,[21] which is usually accompanied by the spiral spin state (SDW whose wave length is as large as the system size). This has been shown for the single-band Hubbard model[22,23] and also for the double-exchange model[20]. It is known[22–24] that the Nagaoka state tends to appear as the ground state when each state on the Fermi surface is occupied by one electron. If we change the boundary condition, the energy of the Nagaoka-Stoner Fermi sea increases due to a change in the momentum of each electron. Then the spiral spin state is energetically favoured because a phase arising from the spiral spin configuration and that from the boundary condition cancel out. In the present case, the same picture seems to determine whether the metallic ferromagnetism occurs in the vicinity of $J = U'$ line.

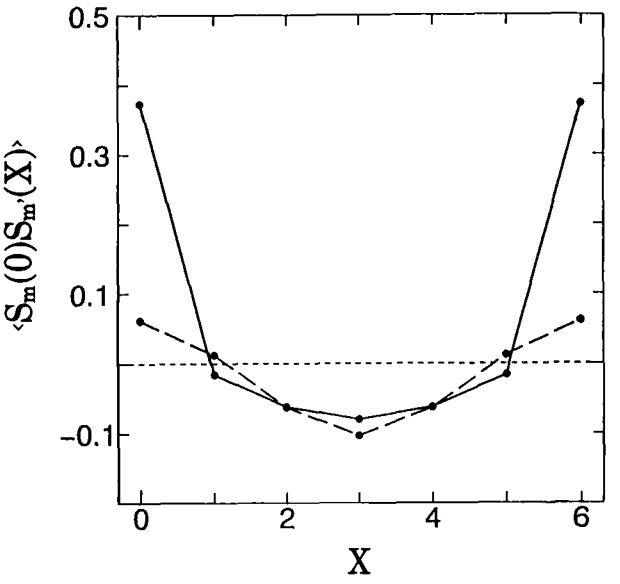

FIGURE 2 The spin-spin correlation function for the ground state in the 6-site system with $U' = J = 100t$ and $\Delta = 0$ in APBC. Solid line and broken line represent the intra ($m = m'$) and inter ($m \neq m'$) orbital correlations, respectively.

Sample size dependence

Next we have to examine the finite size effect. If we compare the two phase boundaries for 6-site and 4-site systems in Figure 1, the dependence of the ferromagnetic region on the boundary condition does tend to decrease with the size. We should note that the effect of changing from PBC to APBC is particularly large for the 4-site system for the following reason. The ferromagnetic region reaches the origin in the parameter space for the 4-site system with APBC because the lowest level of single electron states has a four-fold degeneracy. The ferromagnetic state goes over to one of these degenerate ground states at zero interaction. In order to investigate the finite size effect we need to examine larger systems systematically. If we now go over to the open boundary condition, which should be relevant for isolated molecules, the sample-size-dependence becomes quite small (Figure 3).

The important problem then is whether the ferromagnetic region remains in the thermodynamic limit. The above result, especially that for the open boundary condition, seems to suggest that ferromagnetism will indeed remain in this limit, but

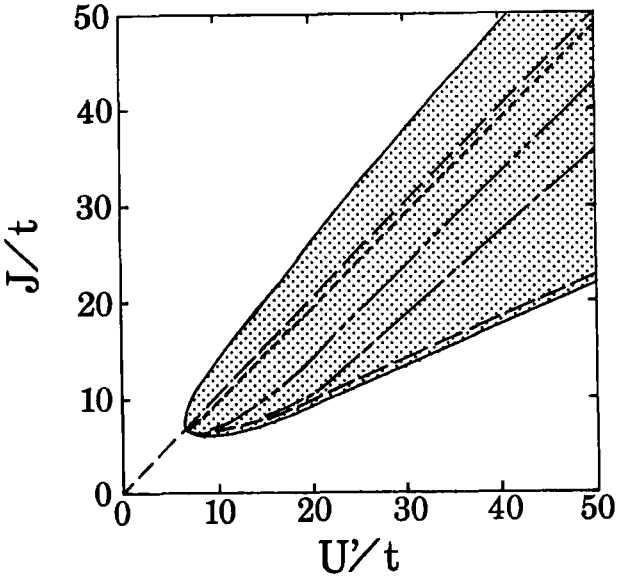

FIGURE 3 The ferromagnetic region for the 6-site system in the open boundary condition with $\Delta = 0$ (shaded area). The lower boundaries of the ferromagnetic phase in the 4-site system with various values of the level offset, Δ, in the open boundary condition are indicated by broken line ($\Delta = 0$), dot-dashed line ($\Delta = t/4$), double-dot-dashed line ($\Delta = t/2$) and dotted line ($\Delta = t$).

this will have to be proven.

Stability of ferromagnetism against the level offset, Δ

In the strong-coupling limit, OSL ferromagnetism will be destabilized when the degeneracy of two levels is lifted. This is because any state with the staggered orbital order has energy higher by $N\Delta/2$ than the configurations where all electrons stay in the lower levels. For the occurrence of the ferromagnetic ground state, the energy gain from the ferromagnetic exchange interaction must be at least larger than this energy gap. Equating $N\Delta/2$ and $2Nt^2/(U'-J)$, we obtain the lower boundary, $J = U' - 4t^2/\Delta$, below which OSL ferromagnetism cannot be realized. The problem now is the robustness of ferromagnetism against the increase in the level offset, Δ, above this line.

The result in the last section shows that we may obtain a reliable picture from the 4-site system if the open boundary condition is adopted. The calculation for this system reveals the following:

(i) The lower boundary of the ferromagnetic phase increases with Δ, up to the line $J = U'$.

(ii) The upper boundary does not shift as Δ is varied.

(iii) The lower boundary is approximately given by the condition that both of the above-mentioned $2t^2/(U' - J) > 4Ut^2/(U^2 - J'^2)$ and $2t^2/(U' - J) > \Delta/2$ are fulfilled.

Even if we include the inter-orbital mixing term, $t_{i,i+1}^{A,B}$, it is difficult to avoid the instability of ferromagnetism against Δ in the conventional perturbational regime. This transfer term produces an inter-site ferromagnetic exchange between two parallel spins in the lower band. However, singlet states simultaneously gain the energy due to antiferromagnetic exchange processes mediated by this mixing term. Thus the ground state would be singlet in the small J region.

We should note that metallic ferromagnetism around the line, $J = U'$, remains stable against Δ as shown in Figure 3. Thus ferromagnetism should be searched in this region where the conventional picture using the second-order perturbation theory fails.

CONCLUDING REMARKS

The occurrence of ferromagnetism requires a fairly large inter-molecular exchange interaction even for the OSL ferromagnetic state.

The phase boundary depends on the boundary condition. This very feature, however, hallmarks metallic ferromagnetism, such as those found in the single-band Hubbard model. The change in the boundary condition in the ferromagnetic metal makes the polarized spin twist.

The ferromagnetic region shrinks with increasing the inter-orbital energy difference. Surviving ferromagnetism is the metallic one.

ACKNOWLEDGMENT

We are very much indebted to Dr A. S. Ichimura for a number of valuable discussions. We also wish to thank Professors Y. Tokura, K. Kubo and Dr K. Kuroki for illuminating discussions. This work was in part supported by a Grant-in-aid from the Ministry of Education.

REFERENCES

1. J. H. Van Vleck, Rev. Mod. Phys. 25, 220 (1953).
2. L. M. Roth, Phys. Rev. 149, 306 (1966); J. Appl. Phys. 38, 1065 (1967).
3. K. I. Kugel' and D. I. Khomskii, Sov. Phys. JETP Lett. 15, 446 (1972); Sov. Phys. JETP 37, 725 (1973).
4. D. I. Khomskii and K. I. Kugel', Solid State Commun. 13, 763 (1973).
5. S. Inagaki and R. Kubo, Int. J. Magn. 4, 139 (1973)
6. M. Cyrot and C. Lyon-Caen, J. Phys. C 6 L.247 (1973); J. de Phys. 36, 253 (1975).
7. S. Inagaki, J. Phys. Soc. Jpn. 39, 596 (1975).
8. H. M. McConnell, Proc. R. A. Welch Found. Conf. Chem. Res. 11, 144 (1967).
9. R. Breslow, Pure Appl. Chem. 54, 927 (1982).
10. J. B. Torrance, S. Oostra and A. Nazzal, Synth. Met. 19, 709 (1986).
11. P. S. Bagus and J. B. Torrance, Phys. Rev. B 39 7301 (1989).
12. E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus and F. Wudl, J. Am. Chem. Soc. 109, 2594 (1987).
13. K. Awaga, T. Sugano and M. Kinoshita, Chem. Phys. Lett. 141, 540 (1987).
14. P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama and M. Kinoshita, Chem. Phys. Lett. 180, 327 (1991).
15. K. Yamaguchi, M. Okumura and M. Nakano, Chem. Phys. Lett. 191, 237 (1992).
16. W. Gill and D. J. Scalapino, Phys. Rev. B 35, 215 (1987).
17. K. Kusakabe and H. Aoki, Physica C 185-189, 1505 (1991).
18. C. Kollmar and O. Kahn, J. Am. Chem. Soc. 113, 7987 (1991).
19. C. Kollmar and O. Kahn, J. Am. Chem. Soc. 113, 7994 (1991).
20. K. Kubo, J. Phys. Soc. Jpn. 51, 782 (1982).
21. Y. Nagaoka, Phys. Rev. 147, 392 (1966).
    D. J. Thouless, Proc. Phys. Soc. London 86, 893 (1965).
    H. Tasaki, Phys. Rev. B 40, 9192 (1989).
22. B. Douçot and X. G. Wen, Phys. Rev. B 40, 2719 (1989).
23. K. Kusakabe and H. Aoki, J. Phys. Soc. Jpn. 61, 1165 (1992); unpublished.
24. M. Takahashi, J. Phys. Soc. Jpn. 51, 3475 (1982)
    J. A. Riera and A. P. Young, Phys. Rev. B 40, 5285 (1989).