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VIEWPOINT

Superconductivity in frustrated systems

Hideo Aoki

Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033, Japan

E-mail: aoki@phys.s.u-tokyo.ac.jp

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Abstract

As a background to the discovery of superconductivity in a pyrochlore-structured transition-metal oxide (KOs_2O_6) by Yonezawa *et al* (2004 *J. Phys.: Condens. Matter* **16** L9), we briefly review why superconductivity in frustrated lattice structures is considered to be intriguing.

There is a mounting body of evidence that the physics of high-T_c superconductivity, or more generally of 'unconventional superconductors', is plunging into a new era in the following sense. First, in the context of materials science, ever since high-T_c superconductivity was discovered in copper oxides by Bednorz and Müller in 1986, one haunting question has been: why cuprates? This question was based on an extensive search by Tokura and co-workers for high-T_c materials, exhausting the transition metal oxides in the periodic table with layered, as well as three-dimensional, perovskite structures, which identified that only the layer-structured cuprate exhibited a high T_c. However, recent years have witnessed that a new surprise was in store for us, when Maeno and co-workers [1] discovered superconductivity in Sr_2RuO_4, which has a crystal structure identical to La_2CuO_4. While Cu and Ru are both transition metals, the cuprate has 3d electrons, and the ruthenate 4d electrons (with different symmetries for the relevant orbit). Although the T_c is not so high for the ruthenate, the surprise is that the superconductivity comes from a time-reversal-broken, spin-triplet pairing, and its mechanism is still under hot debate. Superconductivity in non-Cu oxides was also discovered in $Na_{0.33}V_2O_5$ [2]. Akimitsu and co-workers have discovered superconductivity in MgB_2, where the relevant orbital is p, which is not often evoked for high T_c materials (unless you are talking about doped solid fullerene).

The second sign for a new stage is theoretical: there is an increasing degree of consensus that repulsive electron–electron interaction (which is strong for d electrons), or the electron correlation as it is now termed, causes the high-T_c superconductivity, although non-negligible effects of phonons have been detected. If the electron correlation really is responsible, then it is a natural question to ask whether or how we can possibly enhance the effect by choosing the right, or even exotic, materials. Indeed, a concept that interesting crystal structures can bring about interesting electronic effects is a hallmark of condensed matter physics in recent decades.

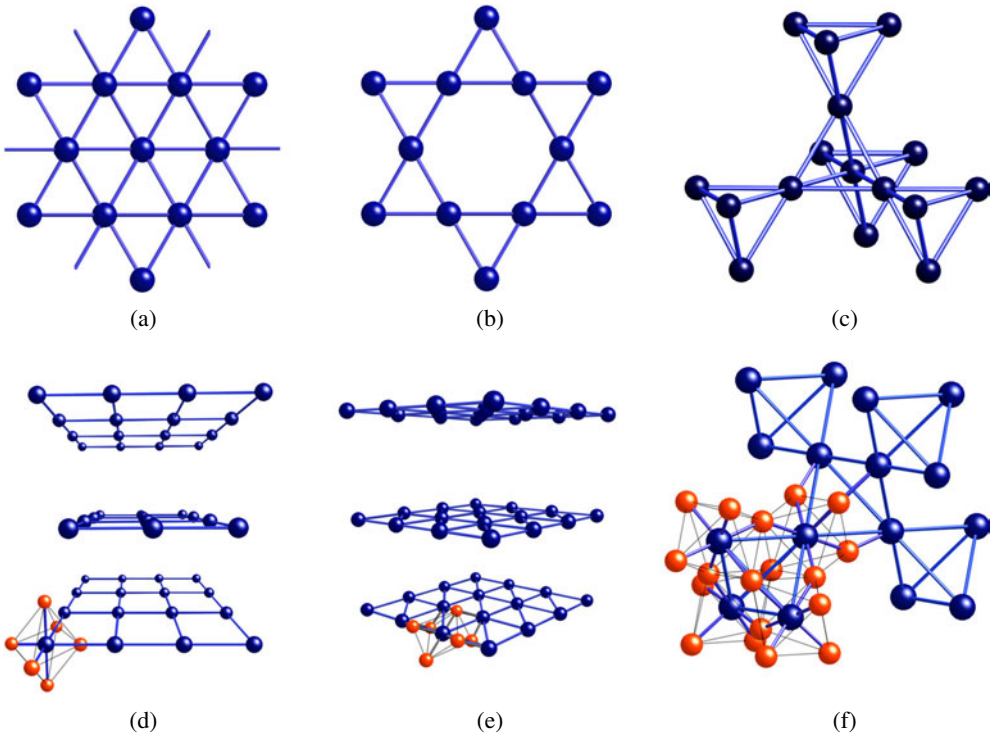

Figure 1. Upper panels: frustrated lattice structures (triangular (a), Kagome (b) and pyrochlore (c)). Lower panels: crystal structures of oxides (cuprate (d; La_2CuO_4), cobalt compound (e; $Na_xCoO_2{\cdot}yH_2O$) and pyrochlore compound (f)). Only the transition metal atoms (black spheres) are displayed, with MO_6 octahedra (white spheres: oxygen atoms) indicated at some places.

Now, Hiroi and co-workers report, in the present issue [3], quite an important discovery of superconductivity with this very aspect. To see its significance, we have to briefly review the underlying physics. The theoretical ideas on electron correlation all started when Anderson wrote the seminal paper on the RVB (resonating valence bond) in the 1970s [4]. He began by noting that, while the ferromagnet is easy to understand (where the spin configuration $\uparrow\uparrow\uparrow\ \cdots$ is a perfectly legitimate quantum mechanical state), the antiferromagnet is very difficult to capture quantum mechanically (in which the classical Néel state $\uparrow\downarrow\uparrow\downarrow\ \cdots$ is illegitimate), and you have in fact to prepare the $S_{\rm total} = 0$ state out of some 10^{23} spins, which involves a vast number of ways of covering the lattice with spin-singlet pairs. Hence significant quantum fluctuations (or RVB states) have to be present in the spin configuration, especially in frustrated lattices such as the triangular one (figure 1(a)), so much so that long-range magnetic orders can even be prohibited, resulting in what is called the spin liquid (just as liquid He is prohibited from forming a solid due to strong zero-point fluctuations in the position of the atoms). Anderson went on to point out that when you dope such a system with carriers (electrons or holes) the system may possibly superconduct. So he extended [5] the idea to the high T_c cuprate, although the relevant CuO_2 plane (figure 1(d)) has a non-frustrated (square) lattice on which the antiferromagnetism resides when undoped. As the holes are introduced into the insulating oxide (which is a 'Mott insulator' due to the electron–electron interaction) the magnetic order disappears, giving way to superconductivity. There is a very heuristic lecture note by Anderson, entitled '50 years of the Mott phenomenon', delivered just after the discovery of the cuprate [6].

Anderson's is indeed a novel idea, which has had a great impact on condensed matter physics. So, while RVB superconductivity *per se* is still somewhat controversial and is being intensively studied, the essence of the idea that the electron–electron interaction (which is the origin of the spin–spin interaction, after all) is at work does seem to hit the right mark in that subsequent works have shown that the repulsive electron–electron interaction can indeed cause superconductivity. Superconductivity from repulsion may at first seem counterintuitive, but that is actually not the case: one way to conceive the pairing is the spin-fluctuation mediated interaction, which can cause the anisotropic Cooper pairs (with a non-zero relative angular momentum ($=2\hbar$ in the cuprate) for the two electrons in a pair) to condense. As for the dimensionality, it has theoretically been suggested that two-dimensional (2D) systems are more favourable than three-dimensional (3D) ones for the spin-fluctuation mediated pairing [7, 8].

Given this background, a question which is still open is: what should happen if you start with a lattice structure in which the configuration $\uparrow\downarrow\uparrow\downarrow\ \cdots$ is just impossible even before you worry about quantum fluctuations? Such a situation is realised in (magnetically) frustrated lattices like triangular, Kagome (figure 1(b)), etc, consisting of triangular plaquettes, where it is simply impossible to put three spins antiferromagnetically ($\begin{smallmatrix}?\\ \uparrow\ \downarrow\end{smallmatrix}$) even for a single plaquette. Statistical mechanics for the classical spins on the frustrated lattices has shown that they have indeed interesting properties (such as the non-collinear (120°) spin structure), and when you move to quantum mechanics the situation becomes a subtle problem of the quantum fluctuations. So the natural question is: would the frustration, accompanied by large fluctuations, favour the magnetic mechanism for superconductivity?

Insulating magnets (where electrons do not move around) on triangular lattices have been well-known and studied for, e.g., $CsCoCl_3$ with a layered structure. For metallic triangular systems (where electrons do move) superconductivity has long eluded realization, but a Japanese group discovered superconductivity in a Co compound, $Na_xCoO_2\cdot yH_2O$ (figure 1(e)) in 2003 [9]. Although T_c ($\simeq$5 K) is not very high, among the interesting features of this material is that superconductivity occurs only when the triangular lattices containing Co are spaced very far apart with the intercalation of water (of all molecules). One intriguing issue is the possibility of the spin-triplet pairing (where the two electrons in a Cooper pair have parallel spins). The triangular lattice affects not only the spin configuration but also metallic band structures, as suggested by a theoretical proposal that the shape of the Fermi surface in the triangular lattice should favour a triplet pairing [10]. So understanding what is happening in the Co compound is a problem for the future. If we turn to wider classes of materials, organic crystals often adopt triangular lattices. Indeed, the organic metal BEDT-TTF family [11] exhibits superconductivity, with T_c rather high for a metal having a small electronic energy scale (band width), and there are theoretical efforts to understand that in terms of correlated electrons on that lattice.

Now, while the triangular lattice is 2D, there is a crystal structure that may be called its 3D realization: the pyrochlore structure (figures 1(c), (f)). Pyrochlore comprises, just as in the perovskite structures, MO_6 (M: transition metal) octahedra, but they are arranged in such a way that the M atoms form a corner-sharing 3D (diamond) network of tetrahedra in place of the corner-sharing 2D network of triangles in triangular and Kagome lattices [12]. A tetrahedron is more frustrated than in a triangle in that you have to worry about frustration for two (rather than one) spins after you put $\uparrow\downarrow$ on an edge, and the spin system on that lattice is indeed shown to be a spin liquid [13]. The frustration, for Ising spins, is also conceived as a 'spin ice' [14]. There have been several interesting works on the metallic behaviour of the pyrochlore compounds. One is the anomalous Hall effect occurring in the Mo compound, which some theorists interpret in terms of the spin chirality [15]. Another is an experimental indication of a heavy-fermion-like behaviour in a vanadate, $Li_2V_2O_4$ [16], having spinel structure that

4	Ti $3d^2$	V $3d^3$				Co $3d^7$		Cu $3d^{10}$
5					Ru $4d^7$			
6				Re $5d^5$	Os $5d^6$			

Figure 2. The elements mentioned in the text displayed in part of the periodic table with d-electron configurations indicated.

contains pyrochlore structure in it. (Talking of spinel, $LiTi_2O_4$ [17] with that structure used to be the highest T_c oxide before the advent of the cuprates.)

So the discovery of superconductivity in a rhenium oxide $Cd_2Re_2O_7$ [18], in 2001, again by Japanese groups (Hiroi and co-workers and independently Yoshimura and co-workers), was remarkable as the first superconducting pyrochlore structure, and provided another 'hot' subject. However, the superconductivity in that material turned out to be a bit of a disappointment in that T_c is $\simeq$1 K, and the pairing (as probed from the spin–lattice relaxation time) does not seem to possess anisotropy, a hallmark for the pairing from electron correlation, which indicates that the superconductivity may not be very out of the ordinary.

That is where the present report by Hiroi and co-workers comes in. They have discovered superconductivity with $T_c \sim 10$ K in an oxide of Os (osmium), KOs_2O_6, with the pyrochlore structure. Os is adjacent to Re in the periodic table for 5d transition metals (figure 2). A metal–insulator (Mott) transition, which is usually considered as an indication of strong electron correlation in transition metal compounds, hence a good sign, was found (at about 230 K) a long time ago [19] for $Cd_2Os_2O_7$, but little else has been known for Os compounds. So this should be an important step forward, certainly in the context sketched above. While the existence of a metal–insulator transition and also a Curie–Weiss behaviour in the magnetic susceptibility [20] observed for the material already indicate that the electrons should be strongly correlated, one promising superconducting property (apart from the higher T_c) Yonezawa *et al* mention is that the upper critical magnetic field, H_{c2}, above which superconductivity (of the second kind) is destroyed, is very large (in contrast to $H_{c2} \simeq 0.3$ T in the Re pyrochlore). If the value exceeds what is called Pauli's limit, which has to be respected if the pairing is conventional spin-singlet, a triplet pairing will be implied.

So there are a lot to be clarified. One immediate question is: why Os? Five-fold degenerate d levels split in crystals into e_g (doubly degenerate) and t_{2g} (triply), where the former are relevant in the cuprate, the latter in the pyrochlore, with different number of electrons occupying the levels (hence different band fillings) between Os and Re. The interplay of such orbital degrees of freedom and spins, incidentally, has been known to accommodate rich phenomena such as the colossal magnetoresistance in Mn oxides. There may also be repercussions on organics [21].

To conclude, the paper by Hiroi *et al* is a significant milestone since it can give important hints as to whether frustration is good news for high T_c superconductivity, so the fascination continues for unconventional superconductivity in exotic structures. The 'Mott phenomenon' does seem likely to enjoy further developments for years to come.

References

[1] Maeno Y *et al* 1994 *Nature* **372** 532
[2] Yamauchi T, Ueda Y and Mori N 2002 *Phys. Rev. Lett.* **89** 057002
[3] Yonezawa S, Muraoka Y, Matsushita Y and Hiroi Z 2004 *J. Phys.: Condens. Matter* **16** L9
[4] Anderson P W 1973 *Mater. Res. Bull.* **8** 153

[5] Anderson P W 1987 *Science* **235** 1196
[6] Anderson P W 1987 *Proc. Int. School of Physics Enrico Fermi* ed R A Broglia and J R Schrieffer (Amsterdam: North-Holland) p 1
[7] Monthoux P and Lonzarich G G 1999 *Phys. Rev.* B **59** 14598
Monthoux P and Lonzarich G G 2001 *Phys. Rev.* B **63** 054529
[8] Arita R, Kuroki K and Aoki H 1999 *Phys. Rev.* B **60** 14585
Arita R, Kuroki K and Aoki H 2000 *J. Phys. Soc. Japan* **69** 1181
[9] Takada K, Sakurai H, Takayama-Muromachi E, Izumi F, Dilanian R A and Sasaki T 2003 *Nature* **422** 53
[10] Kuroki K and Arita R 2001 *Phys. Rev.* B **63** 174507
[11] Singleton J 2000 *Rep. Prog. Phys.* **63** 1111
[12] The name pyrochlore derives from a mineral (a niobium oxide). It may be amusing to remember that minerals exhibit a fascinating variety of structures that could be relevant to physics. For such an idea see, e.g.,
Aoki H, Syono Y and Hemley R J (ed) 2000 *Physics Meets Mineralogy—Condensed-Matter Physics in Geosciences* (Cambridge: Cambridge University Press)
[13] Canals B and Lacroix C 1998 *Phys. Rev. Lett.* **80** 2933
[14] Udagawa M, Ogata M and Hiroi Z 2002 *J. Phys. Soc. Japan* **71** 2365
[15] Taguchi Y, Oohara Y, Yoshizawa H, Nagaosa N and Tokura Y 2001 *Science* **291** 2573
[16] Kondo S, Johnston D C and Jorgensen J D 1997 *Phys. Rev. Lett.* **78** 3729
[17] Johnston D C 1976 *J. Low Temp. Phys.* **25** 145
[18] Hanawa M *et al* 2001 *Phys. Rev. Lett.* **87** 187001
Sakai H *et al* 2001 *J. Phys.: Condens. Matter* **13** L785
[19] Sleight A W *et al* 1974 *Solid State Commun.* **14** 357
[20] Mandrus D *et al* 2001 *Phys. Rev.* B **63** 195104
[21] A '2D pyrochlore structure' has been considered by Arita R, Kuroki K and Aoki H 2000 *Phys. Rev.* B **61** 3207