Theory of the Transition at 0.2 K in Ni-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$

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Abstract

A theory is put forward that the electronic phase transition at 0.2 K in Ni-doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ is result of the formation of a spin density wave in the system of Ni impurities. The driving force for the transition is the exchange interaction between the impurity spins and the spins of the conduction electrons. This creates a small gap at two of the four nodes of the superconducting gap. The effect is to reduce the thermal conductivity by a factor of two, as observed.

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The gap structure of high-temperature superconductors should show up most clearly at low temperatures, when the quasiparticles are located near the nodes. Unfortunately, it is rather difficult to obtain reliable information in this regime, because only relatively few bulk experiments are able to probe properties of the particles and the effect of impurities on them. Among these experiments, thermal conductivity $\kappa_T$ offers the most accurate way of exploring the DC transport properties. Measurements of $\kappa_T$ in Zn-doped YBa$_2$Cu$_3$O$_7$ have confirmed the d-wave nature of the order parameter, while experiments in pure Bi$_2$Sr$_2$CaCu$_2$O$_8$ have shown anomalies in a field whose nature has yet to be resolved.

The effect of impurities on $\kappa_T$ is expected to be particularly informative because of a well-developed theoretical machinery for their calculation. It was therefore particularly surprising that the doped compound Bi$_2$Sr$_2$Ca(Cu$_{1-x}$Ni$_x$)$_2$O$_8$ has an electronic phase transition beginning at a concentration of about $x = 0.006$. As the temperature is lowered through $T^* \approx 0.2\,K$, $\kappa_T$ drops by about a factor of two, indicating a sharp reduction in the density of excited quasiparticles.

The explanation which has been offered for this sharp drop is a transition to a state in which the superconducting order parameter breaks time-reversal symmetry, the $(d_{x^2-y^2} + id_{xy})$ state. This modification is caused by the spin-orbit interaction between the impurity spins and the conduction electrons. In this paper I offer an alternative explanation of the observations based on the exchange interaction between the impurity spins and the conduction electrons which gives rise to a spin density wave (SDW). I shall compare the two theories in the conclusion.

The Hamiltonian is

$$H = H_d - J \sum_i \vec{M}(\vec{R}_i) \cdot \vec{m}(\vec{R}_i),$$

where $H_d$ is the weak-coupling d-wave Hamiltonian and $\vec{M}(\vec{R}_i)$ is the spin of the Ni atom at the impurity site $i$ and $\vec{m}(\vec{R}_i)$ is the spin density of the conduction electrons at the same point. This is the usual exchange interaction. It has been taken as local, but this assumption is not crucial in what follows. Nor is the sign of $J$ important. The system is
treated as two-dimensional.

I propose that there is spiral magnetic order in the impurity spins below $T^*$:

$$\langle \vec{M}(\vec{R}_i) \rangle = \vec{M}(T) \left[ \hat{x} \cos(\vec{Q} \cdot \vec{R}_i) + \hat{y} \sin(\vec{Q} \cdot \vec{R}_i) \right].$$

Furthermore, take $\vec{Q} = (Q/\sqrt{2})(1, -1)$. The reason for this will become clear below. Substitution of Eq. 2 into Eq. 1 shows that there is an effective magnetic field acting on the spins of conduction electrons. It contains two terms. There is a coherent field with wavevector $\vec{Q}$ and a random field arising from the fact that the set $\{\vec{R}_i\}$ is random. I concentrate on the first term here, since it can produce the sudden drop in $\kappa_T$. The effects of the second term are discussed below.

The energy density change in the conduction electron system is

$$\Delta E(\vec{Q}) = -\frac{J^2 M^2 n_{\text{imp}} \mu_B^2}{8} \sum_{\vec{k}} \left[ S(\vec{k} + \vec{Q}) - 1 \right] \chi_m(\vec{k}),$$

where $S(\vec{k})$ is the static structure factor for the positions of the impurities and $\chi_m(\vec{k})$ is the susceptibility of the conduction electrons. $n_{\text{imp}}$ is the two-dimensional density of impurities. In order to determine $\vec{Q}$, this expression must be minimized. The structure factor is that of a highly disordered solid. It will have the peak at $\vec{k} = 0$ required by a sum rule, and other reciprocal lattice vectors (the first at $|\vec{k}| \sim \sqrt{n_{\text{imp}}}$) will be strongly suppressed by the Debye-Waller factor. The susceptibility has an unusual structure in a d-wave superconductor: $\chi_m(\vec{Q}) = a \chi_P \xi_0 |\vec{Q}| + \ldots + (T/\Delta_m) \chi_P (b + c \xi_0^2 |\vec{Q}|^2 + \ldots)$ plus terms higher-order in $T$. $a, b,$ and $c$ are model-dependent constants, $\Delta_m$ is the maximum gap at zero temperature, $\xi_0$ is the coherence length, and $\chi_P$ is the Pauli susceptibility.

At the very low temperatures of interest here, the non-analytic part is the important one. Hence the product $\Delta E(\vec{Q})$ has a minimum at $|\vec{Q}_0| \sim \sqrt{n_{\text{imp}}}$, near the first non-zero peak in $S(\vec{k})$. Physically, the point is this. The dilute system of impurities can only support waves whose wavelength is longer than the interimpurity spacing. The infinite-wavelength ferromagnetic state does not lower the energy of the system because the bulk ferromagnetic susceptibility vanishes. Because $\chi_m(\vec{Q}) \sim |\vec{Q}|$, the system chooses the shortest wavelength
that the dilute impurities will support. The ordering wavevector $|\bar{Q}|$ is small, of order $0.04A^{-1}$. Observe also that if the structure factor is entirely gas-like, then there is no transition. There must be some short-range repulsion between the impurities.

A central point of this paper is that the non-analyticity peculiar to d-wave systems is responsible for the transition. This phenomenon is presumably related to the non-analyticity obtained in calculations of orbital susceptibilities [8]. In s-wave materials, the zero-temperature susceptibility $\chi(\bar{q})$ starts with terms of order $|\bar{q}|^2$: Eq. 1 shows that this will strongly suppress the energy of an SDW in a disordered dilute impurity system. Of course in a dense sublattice of magnetic atoms the situation is different [6] and SDW formation in superconductors has been observed [8].

Considering now the energy $\Delta E$ as an effective interaction in the spirit of RKKY, we can calculate the critical temperature of the SDW in mean-field theory for spin 1 on the Ni site:

$$T^* = \frac{J^2[S(\bar{Q}_0) - 1]\chi_m(\bar{Q}_0)}{12Ak_B\mu_B^2B^2}.$$  

(4)

Here $A$ is the area. Taking $[S(\bar{Q}_0) - 1] = 0.01$, $T^* = 0.2K$, and a susceptibility of $\mu_B^2 \times 1(eV)^{-1}$ per conduction electron, we find a very reasonable value of $J \sim 50meV$ for the exchange constant. However, because we lack precise knowledge of the values of $J$ and $[S(\bar{Q}_0) - 1]$, we cannot use this formula to compare with experiment. Fortunately, most of the unknowns in the theory occur only in the product.

The SDW produces a change in the translation symmetry group. The first Brillouin zone is now a thin slice in momentum space. Two of the nodes [ at $\pm(k_F, k_F)/\sqrt{2}$ ] are in the center of the short axis of the zone and the other two [ at $\pm(k_F, -k_F)/\sqrt{2}$ ] are in indeterminate position. Here $k_F$ is the length of the Fermi wavevector along the diagonal. The states near the former point are strongly affected by the spin ordering because pairs connected by the short reciprocal lattice vector have small energy differences. The states near the other nodes that connected by the short reciprocal lattice vector have large energy differences: this vector is perpendicular to the Fermi surface.
To see the effects on the thermal conductivity, we calculate the quasiparticle energies in
the presence of the coherent part of the effective field in Eq. 1. The expression for these
ergies near a magnetic zone boundary, obtained by diagonalizing the appropriate 4 × 4
matrix, for this is:

\[
E_{\pm}(k_x, k_y) = \pm \frac{1}{2} \{ E^2(\vec{k} + \vec{Q}_0) + E^2(\vec{k}) + 2b_{eff}^2 \pm [(E^2(\vec{k} + \vec{Q}_0) + E^2(\vec{k}))^2
+ 16b_{eff}^2(\xi^2(\vec{k}, \vec{Q}_0) + \Delta^2(\vec{k}, \vec{Q}_0))]^{1/2}\}^{1/2}.
\]

Here \(b_{eff} = JxM\) and \(E^2(\vec{k}) = \xi^2(\vec{k}) + \Delta^2(\vec{k})\), where \(\xi(\vec{k})\) are the normal-state quasiparticle energies referred to the chemical potential and \(\Delta(\vec{k})\) is the d-wave gap function,
while \(\xi_{av}(\vec{k}, \vec{Q}_0) = [\xi(\vec{k} + \vec{Q}_0) + \xi(\vec{k})]/2\) and \(\Delta_{av}(\vec{k}, \vec{Q}_0) = [\Delta(\vec{k} + \vec{Q}_0) + \Delta(\vec{k})]/2\). There
is a level repulsion between the particle-like and hole-like Bogoliubov branches. This
leads to the development of an energy minigap which is obtained from Eq. 3 by setting
\(E(\vec{k}) = \xi(\vec{k}) = \Delta(\vec{k}) = 0\). The result for the minigap energy for the nodes at \(\pm(k_F, k_F)/\sqrt{2}\)
is of order \(b_{eff}^2/v_s Q_0\), where \(v_s\) is the slope of the superconducting energy gap at the node. It
may be estimated as \(v_s \sim \Delta_m/k_F\), where \(\Delta_m\) is the maximum value of the superconducting
gap. Then the minigap is roughly \(10^{-2} meV\) when \(M = 1\). The corresponding gap at the
other pair of nodes located at \(\pm(k_F, -k_F)/\sqrt{2}\) is much smaller, of order \(b_{eff}^2/v_F Q_0\), where
\(v_F\) is the Fermi velocity. The big minigap is of order \(T^*\), while the latter is smaller by a
factor of about 30. As a result, the system develops an appreciable gap in two of its nodes
at the transition, while the other two remain essentially ungapped at \(T^*\).

The thermal conductivity may then be calculated in the presence of \(M(T)\), which is
again obtained from spin one mean field theory. The result from the standard Boltzmann
equation approach is shown together with the data from a sample with \(x = 0.015\) in Fig.
1. The curve has been fit from \(0.1K\) to \(0.3K\) using as adjustable parameters the quantities
\(Q_0, T^*, \text{ and } b_{eff}\), with the results \(Q_0 = 24k_B T^*/v_s \sim k_F/50\), \(T^* = 0.22K\), and \(b_{eff} = 8k_B T^*\).
The fact that the fit parameters are in good agreement with the \textit{a priori} estimates above is
strong evidence for the correctness of the theory. To the extent that the specific heat can
be measured, the entropy change in the same temperature range changes by about \(N_{imp} \ln 3\),
which is consistent with this picture.

The fit in Fig. 1 is poor at low temperatures owing to the neglect of the random term in the effective field. It is known that this randomness leads to a crossover from the clean result $\kappa_T \sim T^2$ at high temperatures to $\kappa_T \sim T$ at low temperatures. This effect is present in the data in Fig. 1, though in a temperature regime where the data look noisy. The linear regime is not present in the theory as it stands. Improvements in this direction are relatively straightforward and will be presented in a longer paper. At higher temperatures the data follow a law $\kappa_T \sim T^\alpha$ with $\alpha \approx 1.6 - 1.75$, whereas the current theory gives the usual result $\alpha = 2$. There is no theory of this intriguing observation at the present time. The corresponding exponent in Zn-doped YBa$_2$Cu$_3$O$_7$ appears to greater than 2.

Considered at the Ginzburg-Landau level, the present theory has the structure:

$$F = a_M(T)M^2 - a_{Mm}Mm + a_m m^2 + O(M^4, M^2 m^2, m^4).$$

The order parameters $M$ and $m$ represent the amplitude of the SDW on the impurities and on the conduction electrons respectively. The coefficient $a_M(T)$ is entirely of entropic origin, implying $a_M(T) \geq 0$, as the direct interaction between the impurity spins is negligible ($\mu_B n_{imp}/k_B \sim 10^{-4}K$). The temperature dependence of the other two coefficients $a_{Mm}$ and $a_m$ may be neglected, as they are proportional to the exchange coupling and the inverse zero-temperature bulk susceptibility, respectively. The transition takes place when the lowest eigenvalue of the quadratic form changes sign: this is the equation for $T^*$ given above. This treatment makes it clear that the SDW involves the ordering of both the impurity spins and the conduction electrons. In this regard, the present picture resembles that put forward by Balatsky [5], which postulates a time-reversal symmetry breaking superconducting order parameter $(d_{x^2-y^2} + id_{xy})$. However, the resemblance is superficial. In the $(d_{x^2-y^2} + id_{xy})$ theory, the Ginzburg-Landau expansion has the

$$F = a_M(T)M_z^2 + \alpha_0 |\Delta_0|^2 + \alpha_1 |\Delta_1|^2 + ib_{M\Delta}M_z(\Delta_0\Delta_1^* - \Delta_0^*\Delta_1) + O(M_z^4, \Delta_0^4, \Delta_1^4)$$

Here $\Delta_0$ and $\Delta_1$ are the $d_{x^2-y^2}$ and $d_{xy}$ superconducting order parameters and $M_z$ is the amplitude of the uniform magnetization on the impurity sites. The most important difference
from the free energy in Eq. (1) lies in the fact that the coupling term is trilinear. As a result, the phase transition can only arise from a change of sign in $a_M(T)$. In view of the estimate of the direct magnetic coupling given above, this is unlikely to occur at the temperatures in question. The two theories differ also in their predictions for $\kappa_T$. In the SDW theory, only one half of the nodes are substantially gapped, leading to a natural explanation of the sudden drop by a factor of two. In the $(d_{x^2-y^2} + id_{xy})$ theory all nodes are gapped. The theory must rely on the formation of an impurity band of states in the gap to explain the low temperature limit. This would imply that the zero-temperature limit of $\kappa_T/T$ is extrinsic, depending on the impurity concentration. The fact that $\kappa_T/T$ approaches a value comparable to the universal limit makes this explanation unattractive, but it is clearly consistent with the SDW theory.

In closing it is appropriate to consider how to sharpen the comparison of experiment and theory. The two-dimensional SDW transition of course needs to be stabilized by interlayer coupling. It is not clear what the three-dimensional ordering will be, as the dipole or other coupling may then compete with RKKY. In any case, the small impurity concentrations may make the determination of the structure by neutron scattering difficult. A further complication is the dependence of $T^*$ on the structure factor. This can cause the transition temperature to depend on the preparation method and annealing time. It could be responsible for the fact that the transition temperatures in samples of Bi$_2$Sr$_2$Ca(Cu$_{1-x}$Ni$_x$)$_2$O$_8$ with nominal compositions $x = 0.006$ and $x = 0.015$ are about the same. It is likely that a different mechanism suppresses the transition at $x = 0.024$. At these higher concentrations $\chi_m(q = 0, T = 0)$ will become appreciable due to the random interaction term. This will favor a transition into a ferromagnetic state, as there is always a $\delta^2(\vec{k})$ term present in $S(\vec{k})$. Repeating the calculation of the quasiparticle energies as above shows that this does not produce any gap in the quasiparticle spectrum and thus would not be seen in $\kappa_T$. By the same token, application of a uniform magnetic field produces a first-order transition to a ferromagnetic state and erases the $\kappa_T$ anomaly, as is seen in the experiments. A simple way to distinguish between the SDW and $(d_{x^2-y^2} + id_{xy})$ theories experimentally is that the SDW
responds isotropically to an applied field, while the \((d_{x^2-y^2} + id_{xy})\) would predict the disappearance of the \(\kappa_T\) anomaly only if the field is in the basal plane. Furthermore, the SDW would lead to transport anisotropy between the \((1,1)\) direction and the \((1,-1)\) directions, if domain effects can be eliminated. This could happen automatically if there is coupling of the SDW to the superlattice distortion in the crystal structure.

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REFERENCES

[1] L. Taillefer et al., Phys. Rev. Lett. 79, 483 (1997).

[2] K. Krishana, N.P. Ong, Q. Li, G.D. Gu, and N. Koshizuka, Science 277, 83 (1997); H. Aubin, K. Behnia, S. Ooi, and T. Tamegai, Science 280, 11 (1998); K. Krishana et al., Science 280, 11 (1998).

[3] Y. Sun and K. Maki, Europhys. Lett. 32, 355 (1995); M.J. Graf et al., Phys. Rev. B 53, 15147 (1996); M.R. Norman and P. Hirschfeld, Phys. Rev. B 53, 53706 (1996).

[4] R. Movshovich, M.A. Hubbard, M.B. Salamon, A.V. Balatsky, R. Yoshizali, J.L. Sarrao and M. Jaime, Phys. Rev. Lett. 80, 1968 (1998); R. Movshovich, M. Jaime, M.A. Hubbard, M.B. Salamon, A.V. Balatsky, R. Yoshizali, and J.L. Sarrao, J. Phys. Chem. Sol. 59, 2100 (1998).

[5] A.V. Balatsky, Phys. Rev. Lett. 80, 1972 (1998); A.V. Balatsky, J. Phys. Chem. Sol. 59, 1689 (1998).

[6] See, e.g., Theory of Simple Liquids, J.-P. Hansen and I.R. McDonald (Academic Press, London, 1986)

[7] P.W. Anderson and H. Suhl, Phys. Rev. 116, 898 (1959).

[8] L.N. Bulaevskii, A.I. Buzdin, M.L. Kulik, and S.V. Panjukov, Adv. Phys. 34, 175 (1985) is a review.

[9] S.K. Yip and J.A. Sauls, Phys. Rev. Lett. 69, 2264 (1992).
FIGURES

FIG. 1. Comparison of theory (solid line) and experimental data (points) for the thermal conductivity divided by temperature versus temperature. The data are taken from Ref. 4.
\[ \frac{\kappa_r}{T} \text{ (W/K}^2\text{ m)} \]

\[ T \text{ (K)} \]