Real-Space and $\vec{k}$-Space Electron Pairing in $BaPb_{1-x}Bi_xO_3$

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(Received 12 June 1981)

A theory of the condensation of electrons, coupled strongly to optic phonons, into a lattice of real-space electron pairs is presented. Even if the on-site interaction is repulsive, real-space pairing of the Anderson form may occur because of interaction with other sites. Dilution weakens the intersite interaction and causes a phase transition that may be to a metallic state which undergoes $\vec{k}$-space (BCS) pairing at low temperatures. The results are applied to $BaPb_{1-x}Bi_xO_3$.

PACS numbers: 71.30.+h, 71.38.+i, 74.10.+v

In the BCS theory of superconductivity[1] the electron-phonon interaction causes electrons at the Fermi surface in states $(\vec{k}, \sigma)$ and $(-\vec{k}, -\sigma)$ to pair. Anderson[2] has proposed that, as the strength of the electron-phonon coupling is increased, it could overcome the Coulomb repulsion between electrons leading to a pairing of electrons in real space. In this Letter the theory of the formation of a lattice of such electron pairs is presented. We consider a half-filled band of electrons coupled strongly to optic phonons. Even if the effective on-site interaction between electrons is repulsive, a real-space pairing of the Anderson form may occur because of intersite interactions. Dilution of the lattice causes a transition from the real-space paired state to a state which may be metallic and undergo BCS pairing at low temperatures. We propose that such a transition occurs in the $BaPb_{1-x}Bi_xO_3$ alloy system.

In this system the Pb and Bi atoms occupy a simple cubic lattice with an O atom between each pair. There is one conduction electron per Bi^{4+} ion which will be in the nonbonding 6*s* state. The compound $BaBiO_3$ is a semiconductor with the valence configuration $Ba_2Bi^{3+}Bi^{5+}O_6$.[3] We show that this valence ordering can be viewed as a lattice of Anderson electron pairs which is stabilized by polarizing the O octahedra. As the temperature is increased, there is evidence[3] of a phase transition to a cubic structure at $T \sim 800$ K. We show that this transition, too, can be understood within the model of a lattice of Anderson electron pairs. The substitution of Pb dilutes the Bi lattice and leaves one electron per Bi atom. The semiconducting state persists[4] up to a concentration of 65% Pb—an observation which favors a local description rather than a charge-density-wave description.[5] At concentrations in excess of 65% Pb the alloys are poor metals but high-temperature superconductors.[4]

Consider first $BaBiO_3$. The energy to displace each O atom by x can be written as[2]

$$E_{ab}(x) = \tfrac{1}{2} C x^2 - g x (q_a - q_b), \tag{1}$$

where $q_a - q_b$ is the charge difference between the two nearest-neighbor Bi atoms and g and C are coupling constants. Minimizing E_{ab} with respect to x for fixed q_a and q_b gives rise to a nearest-neighbor interaction, and the complete Hamiltonian that describes the conduction electrons in the Bi 6*s* band is

$$H = \sum_{\substack{\langle ij \rangle \\ \sigma}} t c_{i\sigma}^{\dagger} c_{j\sigma} - \frac{g^2}{2C} \sum_{\langle ij \rangle} (q_i - q_j)^2 + \sum_i U_c n_{i\uparrow} n_{i\downarrow} + \sum_{ij} \frac{e^2}{\epsilon r_{ij}} q_i q_j . \tag{2}$$

The $n_{i\sigma}$ are electron numbers on each site; the first term describes electron transfer between nearest-neighbor sites $\langle ij \rangle$, and the next two, the intrasite and intersite Coulomb interactions.

A magnetic analog can then be derived. For $BaBiO_3$, $q_i = 1 - n_{i\uparrow} - n_{i\downarrow}$, and putting $m_i = n_{i\uparrow} + n_{i\downarrow} - 1$ gives a "spin" variable with the states $m_i = \pm 1$ (each singly degenerate) and $m_i = 0$ (doubly degenerate). To include conservation of electron number, a chemical potential or magnetic field must be added, but since there is one 6*s* electron per Bi atom, $\sum m_i = 0$ and the total magnetic field is zero. For simplicity, the intersite Coulomb interaction will be replaced by the short-range interaction $e^2 \alpha / 6 \epsilon a$ [α is the Madelung constant (1.75 for simple cubic); a is the lattice parameter]. In the small-bandwidth limit the Hamiltonian (2) then becomes

$$H=\Delta\sum_i m_i^2+J\sum_{\langle ij\rangle} m_i m_j, \qquad (3)$$

where $\Delta=\frac{1}{2}(U_c-6g^2/C)$ and $J=g^2/C+e^2\alpha/6\epsilon a$. This is now of the Blume-Emergy-Griffiths (BEG) form[6] with the states $m_i=+1$, 0, and -1 denoting Bi^{3+}, Bi^{4+}, and Bi^{5+}.

This reduced Hamiltonian implies, firstly, that if $\Delta/zJ<\frac{1}{2}$ (z is the coordination number), the ground state will be "antiferromagnetic" and will consist of electron pairs ($m=+1$) alternating with empty sites ($m_i=-1$). In particular, if $\Delta<0$, the ground state is a regular array of coupled Anderson "negative U" centers. If $\Delta/zJ>\frac{1}{2}$, the ground state has a single electron ($m_i=0$) on each site.

Secondly, at finite temperatures, there are two types of excitations from a paired ground state. Single-particle excitations have the smaller energy and break up electron pairs into two singly occupied sites ($m_i=\pm1\rightarrow m_i=0$). Two-particle excitations in which the long-range order of the paired sites is disrupted ($m_i=\pm1\rightarrow m_i=\mp1$) are also present. In both excitations the O atoms have relaxed to equilibrium positions.

Thirdly, the BEG model is known[6] to exhibit a phase transition, the nature of which depends on the value of Δ/zJ. In the hypothetical limit $\Delta/zJ\sim-\infty$, most of the electrons remain paired ($m_i=\pm1$), resulting in a second-order, order-disorder transition driven by two-particle excitations; i.e., the regular array of Anderson electron pairs melts.[7] As Δ/zJ increases through zero, the transition is increasingly dominated by single-particle excitations. For $\frac{1}{2}>\Delta/zJ>$const ($=\frac{1}{3}\ln2$ in mean-field theory) it is first order with a discontinuous drop in the number of electron pairs. For all Δ/zJ, all Bi sites are equivalent in the high-temperature phase and the system will be cubic, as experiment indicates.[3]

The phase boundary of the Hamiltonian (3), calculated within mean-field theory for $z=6$, is shown in Fig. 1. The transition is second- or first-order according as Δ/zJ is less or greater than $\frac{1}{3}\ln2$. Also shown in Fig. 1 is T_c calculated from a Hartree approximation directly on Eq. (2). This approximation includes only unrelaxed single-particle excitations, and so is only reasonable when $\Delta/zJ\gtrsim0$.

Consider now the effect of replacing some Bi by Pb and assume for simplicity that Pb sites are always Pb^{4+} (i.e., $q_{Pb}=0$). Substituting into both the electron-phonon and intersite Coulomb terms of (2) then reproduces the Hamiltonian (3) except that every Pb site is an inert, nonmagnetic ($m_i=0$) impurity. Thus $BaPb_xBi_{1-x}O_3$ is modeled by a dilute magnetic system of the BEG form. Long-range forces, such as the Coulomb interactions present here, tend to suppress the effect of concentration fluctuations. As a preliminary model, it will therefore be assumed that alloying with Pb simply reduces the coordination number z of the lattice.

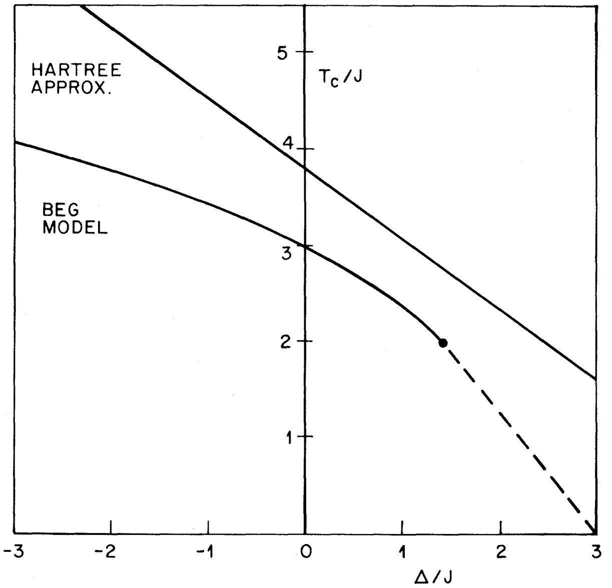

FIG. 1. T_c as a function of Δ/J calculated in the Hartree approximation to Eq. (2) in the zero-bandwidth limit (upper curve) and in the mean-field approximation on the BEG model, Eq. (3) (lower curve). Solid lines denote second-order and dashed lines first-order transitions and the dot, a tricritical point. In the Hartree calculation U and $e^2/\epsilon a$ were fixed at values of 2 and 1, respectively, and g^2/C varied.

If $\Delta<0$, both the site and bond terms in (3) favor pairing and a line of second-order phase transitions in the (T, z) plane is expected, with $T_c\rightarrow0$ as $z\rightarrow z_c$, a percolation limit.

If $\Delta>0$ the site term favors unpaired electrons while the bond term favors pairing. In this case the reduction of z reduces the number of bonds per site and hence increases the relative importance of the site term. Thus by decreasing the average value of Δ/zJ, dilution can drive the transition first order. At $T=0$, the boundary between the paired state and the unpaired state is then at $z_c=2\Delta/J$.

Since each unpaired electron can have its spin

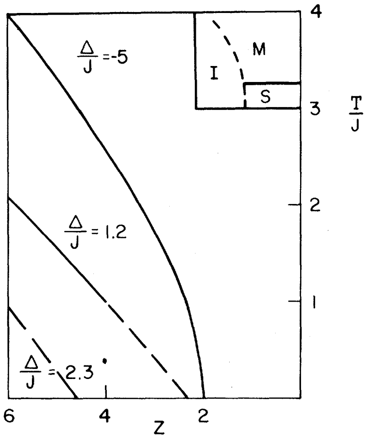

FIG. 2. T_c as a function of the average coordination number z ($=6x$) in the alloy series $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$ for different values of Δ/J. T_c is calculated in the Bethe-Peierls approximation. The inset shows schematically the effect of a metallic state on the region $T_c\to 0$, $z\to z_c$ for $\Delta/J>0$ with a triple point where the three phases I (paired and insulating), M (single-particle and metallic), and S (metallic and BCS superconducting) come together.

either up or down, the unpaired state has a finite zero-point entropy which dominates all other free-energy terms at low temperatures. A first-order phase boundary of T_c/J plotted against z therefore has a slope of $(2\ln 2)^{-1}$ at $T_c=0$, $z_c=2\Delta/J$. We have extended the results to higher temperature by using a Bethe-Peierls approximation,[8,9] treating a central "spin" coupled to z neighbors, each of the latter being coupled to a Bethe-Peierls "field," B. Both the first- and second-order transitions separate two regions where the average sublattice "magnetization" is zero and finite, respectively. The self-consistency condition used to determine B was therefore $\langle m_0\rangle(B)=-\langle m_j\rangle(B)$, where the brackets denote thermal expectation values. The results are shown in Fig. 2. The Bethe-Peierls approximation correctly gives the low-temperature behavior of the first-order transitions and gives a lower value of T_c than mean-field theory.

To relate the above analyses to the onset of BCS pairing we must consider the effect of the hopping term in Eq. (2). Firstly, will the transition described above be, at $T=0$, an insulator-metal transition? In the paired state with $z=6$, both single- and two-particle excitations can propagate only through higher-energy intermediate states, leading to a narrowed bandwidth, e.g., for single-particle excitations, $W_p\sim 2zt[5t/(2zJ-2\Delta)]$. As z decreases due to dilution, single-particle excitations can propagate through Pb sites, leading to a bandwidth $W_p\sim 2(6-z)t$. If a gap is to be retained between this empty band and the filled Bi band then $\frac{1}{2}W_p<t_0-2\Delta+(z-3)g^2/C+ze^2\alpha/6\epsilon a$, where t_0 is the energy difference between Pb and Bi sites. Turning now to the limit $z\to 0$, the Bi impurities in BaPbO_3 will behave as usual donors if $\Delta>0$, with a Mott transition at some value of z. If $\Delta<0$, there is the possibility of charge disproportionation into Bi^{3+} and Bi^{5+} states. This requires that an electron can bind to the short-range potential at a Bi^{4+} site. Such binding will not occur if $12t>t_0+2|\Delta|$. Thus, the transition with decreasing z in Fig. 2 can be from an insulator to a metal only if $|\Delta|$ is not too large.

The hopping term will affect the phase diagram in Fig. 2. In the conventional theory of the metallic state the electron-phonon interaction gives only a small contribution to the energy[10] which is dominated by the energy lowering due to the hopping term. The result will be to shift the boundary of the metallic state in Fig. 2 to larger values of z_c. Furthermore, the spin degeneracy of the unpaired state is removed and the corrections to the free energy go as T^2, causing the phase boundary to rise perpendicular to the $T=0$ line (see inset). The question of precursor effects in the metallic state is of interest in view of the high resistivity found experimentally and requires further work.

A metallic state will undergo a BCS transition to the superconducting state. At the transition to real-space pairing the dimensionless electron-phonon coupling constant λ is about 1 [$\lambda=3N(E_\mathrm{F})\times g^2/C$ with $N(E_\mathrm{F})$ as the density of states] and as a result the BCS transition temperature will be relatively high. BCS pairing in the metallic state involves virtual interaction with phonons whereas real-space pairing is stabilized by static displacements. In BCS pairing all integrals are cut off at ω_0 (the O optic mode energy) and the BCS coherence length $\xi\sim(E_\mathrm{F}/\omega_0)a$ when $\lambda\sim 1$. As a result the transition to real-space pairing takes place at values of $\xi\gg a$.

The model discussed here is closely related to the theory of bipolarons[11,12] with pairing between nearest-neighbor sites rather than on-site pairing discussed here. Chakraverty[11] has discussed the transition from such a bipolaronic state to a metallic state as the electron-phonon coupling strength decreases and pointed out that the metallic state would be a high-temperature BCS superconductor. Recently Alexandrov and Ranninger[12] have discussed a possible Bose condensation of bipolarons. At present the best example of bipolarons occurs in Ti_4O_7,[13] which, however, does not show superconductivity.

In summary, we have discussed the transition between real-space and $\vec{k}$-space electron pairing that can occur with alloying in a material with strong coupling of the conduction electrons to optic phonons. We propose $BaPb_{1-x}Bi_xO_3$ as an example. Alloys with $x<0.35$ are high-T_c superconductors[4] while those with $x>0.35$ are semiconductors. The valence configuration[3] $Ba_2Bi^{3+}Bi^{5+}O_6$ can be viewed as an ordered array of Anderson electron pairs and the persistence of semiconducting behavior over a wide range of alloying supports a local model of electron pairs. Further investigation, especially of the magnetic properties, of this alloy series would be helpful.

The authors are grateful to P. W. Anderson, B. Batlogg, and R. A. Pelcovits for useful conversations and to C. DiCastro and J. Ranninger for a helpful discussion of the relation of the BEG and Hubbard models. This work was supported in part by the U. S. Office of Naval Research, Contract No. N00014-77-C-0711.

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 106, 162 (1957), and 108, 1175 (1957).

[2] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[3] D. E. Cox and A. W. Sleight, Acta Crystallogr. Sect. B 35, 1 (1979).

[4] T. D. Thanh, A. Koma, and S. Tanaka, Appl. Phys. 22, 205 (1980).

[5] For a semiconducting charge-density-wave state to survive a large reduction in carrier density, a very special Fermi surface and a considerable change in the wave vector are required. The local model presented here requires neither.

[6] M. Blume, V. J. Emery, and R. B. Griffiths, Phys. Rev. A 4, 1071 (1971).

[7] The Verwey transition in Fe_3O_4 is believed to be an example of such a charge-disordering transition.

[8] H. A. Bethe, Proc. Roy. Soc. London, Ser. A 150, 552 (1935).

[9] T. A. L. Ziman and R. J. Elliott, J. Phys. C 13, 845 (1980).

[10] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, *Quantum Field Theoretical Methods in Statistical Mechanics* (Pergamon Press, New York, 1965).

[11] B. K. Chakraverty, J. Phys. (Paris) Lett. 40, L-99 (1979).

[12] A. Alexandrov and J. Ranninger, Phys. Rev. B 23, 1796 (1981), and to be published.

[13] C. Schlenker, S. Ahmed, R. Buder, and M. Gourmala, J. Phys. C 12, 3503 (1979).