Resonating-valence-bond state with charge degrees of freedom in Sm_3Se_4

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The unusual properties of the intermediate-valence semiconductor Sm_3Se_4 (the absence of a charge ordering and the giant linear term in the specific heat) are explained on the basis of a model of a pseudospin quantum fluid.

Anderson's theory of resonating valence bonds (the RVB theory) for high-temperature metal oxide superconductors[1] has recently attracted much more interest to the problem of the ground state of quantum-mechanical spin systems. It has been suggested that, at least for certain lattices, a spin-liquid state with properties differing markedly from those of an ordinary antiferromagnetic state arises. Despite the absence of free current carriers, there is a Fermi surface in these systems, so there is a linear term in the specific heat, γT. Neither the experimental data on the specific heat of the high-temperature superconductors[2,3] nor the results of Monte Carlo calculations for the Heisenberg and Hubbard models[4,5] have completely resolved the question of whether an RVB state can be realized. In the present letter we present arguments for the case that a state analogous to an RVB state can arise in systems with charge degrees of freedom and that such a state apparently exists in Sm_3Se_4.

In this compound the Sm^{2+} and Sm^{3+} ions are distributed among crystallographically equivalent sites in a lattice of the Th_3P_4 type. In contrast with the isostructural compound Eu_3S_4, there is no hint of a charge ordering anywhere down to $T=0$ (Refs. 6 and 7). The compound Sm_3Se_4 is a semiconductor in which a hopping conductivity operates on the basis of the $4f$ states of Sm; f-d hybridization effects, which are important for other intermediate-valence compounds of Sm, are inconsequential, since the $5d$ band lies 1 eV above E_F. A giant linear term in the specific heat was recently discovered[8] in Sm_3Se_4 at $T \lesssim 1$ K, with $\gamma \approx 4.5$ J/(mole·K^2). This term is even larger than those in heavy-fermion systems. This fact, combined with the absence of a charge ordering, suggests, by analogy with Ref. 1, the realization of an RVB state.

We know that a prerequisite for the appearance of an RVB state is the existence of frustrations (e.g., equilateral triangles in models with an antiferromagnetic exchange interaction of nearest neighbors). Let us examine a simple model with charge frustrations. We assume that in each unit cell **R** there is an equilateral triangle (sites $i = 1,2,3$). We assume that the integrals representing transport between cells, $t_{ij}^{\mathbf{RR}'}$ are small in comparison with the transport integral τ and the Coulomb interaction (V) between the sites of a cell. We ignore the Coulomb interaction between cells, while we assume that the repulsion at each site is infinite. We can thus switch to a model of spin-zero fermions:

$$H = H_0 + H_1 = \sum_{\mathbf{R}} H_{\mathbf{R}} + \sum_{\mathbf{R} \neq \mathbf{R}'} t_{ij}^{\mathbf{R}\mathbf{R}'} c_{\mathbf{R}i}^{+} c_{\mathbf{R}'j} \quad ,$$

$$H_{\mathbf{R}} = \sum_{i \neq j} (\tau c_{\mathbf{R}i}^{+} c_{\mathbf{R}j} + V c_{\mathbf{R}i}^{+} c_{\mathbf{R}i} c_{\mathbf{R}j}^{+} c_{\mathbf{R}j}). \tag{1}$$

We assume that the number of electrons is equal to the number of unit cells. The Hamiltonian $H_{\mathbf{R}}$ is diagonalized by introducing some new annihilation operators $c_\alpha = \Sigma_i U_{\alpha i} c_i$,

$$c_0 = (c_1 + c_2 + c_3)/\sqrt{3}; \quad c_+ = (c_1 - c_2)/\sqrt{2}; \quad c_- = (c_1 + c_2 - 2c_3)/\sqrt{6}; \tag{2}$$

$$H_{\mathbf{R}} = 2\tau c_{\mathbf{R}0}^{+} c_{\mathbf{R}0} - \tau \sum_{\alpha = \pm} c_{\mathbf{R}\alpha}^{+} c_{\mathbf{R}\alpha} + (V/2) n_{\mathbf{R}} (n_{\mathbf{R}} - 1); \quad n_{\mathbf{R}} = \sum_{\alpha} c_{\mathbf{R}\alpha}^{+} c_{\mathbf{R}\alpha} \quad . \tag{3}$$

At $\tau > 0$ the ground state is thus doubly degenerate. Applying an ordinary operator perturbation theory in $t_{ij}^{\mathbf{R}\mathbf{R}'}$ (as in the derivation of the kinetic antiferromagnetic exchange in the polar model[10]), we find the following expression for the effective Hamiltonian of the interaction of the cells:

$$H_{int} = PH_1 \frac{1}{E_0 - H_0} H_1 P = \sum_{\mathbf{R}\mathbf{R}'} J_{\mathbf{R}\mathbf{R}'}^{ab} \mathbf{S}_{\mathbf{R}}^{a} \mathbf{S}_{\mathbf{R}'}^{b} + \ldots \qquad (a, b = x, y, z) \quad , \tag{4}$$

where the operator P projects onto states with a single electron in each cell, $\mathbf{S}_{\mathbf{R}} = \frac{1}{2}\Sigma_{\alpha,\beta = \pm} c_{\mathbf{R}\alpha}^{+} \vec{\sigma}_{\alpha\beta} c_{\mathbf{R}\beta}$ ($\vec{\sigma}$ are the Pauli matrices) are pseudospin operators, and

$$J_{\mathbf{R}\mathbf{R}'}^{ab} = (1/4V) \mathrm{Tr} (\sigma^a \tilde{t}^{\mathbf{R}\mathbf{R}'} \sigma^b \tilde{t}^{\mathbf{R}'\mathbf{R}}), \qquad \tilde{t}_{\alpha\beta}^{\mathbf{R}\mathbf{R}'} = \sum_{ij} U_{\alpha i} U_{\beta j} t_{ij}^{\mathbf{R}\mathbf{R}'}$$

(the trace is taken over the indices $\alpha = \pm$). Expression (4) is quadratic in the pseudospins of the Hamiltonian of the most general type. For specific lattices, it can be simplified. For example, if the triangles are stacked one atop another, or rotated 60° with respect to each other, we would have $t_{ij} = t\delta_{ij}$ or $t_{ij} = t(1 - \delta_{ij})$ in the nearest-neighbor approximation, and in both cases Hamiltonian (4) would reduce to an isotropic Heisenberg Hamiltonian.

It is not difficult to see that a charge ordering corresponds to a state with $\langle \mathbf{S}_{\mathbf{R}} \rangle \neq 0$. Because of the frustrations, the ordered state may be disrupted both for two-dimensional lattices and (in principle) for three-dimensional lattices,[1] in a process accompanied by the formation of a pseudospin liquid. The anisotropy of Hamiltonian (4) is no obstacle here.[9] In an RVB state we have $\gamma \sim 1/J$ (Ref. 1), and this quantity can be very large since $|t_{ij}^{\mathbf{R}\mathbf{R}'}|$ is small.

This model is of course an overly crude approximation of the actual Th_3P_4 structure, but the latter does contain nearest-neighbor triangles, and with certain relations among the parameters, which we are assuming prevail in Sm_3Se_4, the latter structure may be frustrated.

Also of major interest is a report[11] of an increase in γ from 200 to 400 mJ/(mole·K^2) in the $Yb_4As_{3-x}P_x$ system as x is increased from 0 to 0.3 (the concentration of current carriers does not change substantially in the process, remaining at the level of 10^{-3} per atom). The compound Yb_4As_3 has an anti-Th_3P_4 structure and undergoes a charge ordering near 300 K, accompanied by a structural transition.[12] It is possible that doping with phosphorus intensifies the quantum-mechanical effects and disrupts the ordered state (by analogy with the doping of La_2CuO_4 with strontium?).

We note in conclusion that although the status of the RVB theory in connection with the problem of high-temperature superconductivity is still unclear, the existence of high-temperature superconductors without magnetic ions ($BaPb_{1-x}Bi_xO_3$, $K_{1-x}Ba_xBiO_3$) is not an unambiguous argument against this theory, since an RVB state might be realized in such superconductors on the basis of charge fluctuations, rather than spin fluctuations [corresponding, for example, to a $Ba_2(Bi^{3+}Bi^{5+})O_6$ ordering[13]].

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