Robinson and Friedberg,[6] Kapadnis and Hartmans,[4] and Spence *et al.*[7]

It is of further interest to observe that the Néel temperature for the present compound is higher than the corresponding $CoCl_2 \cdot 6H_2O$, whose Néel temperature is 2.29°K. This difference in transition temperature for the bromine and chlorine salts has also been observed by others[4,6,7] in the case of manganese and nickel, in each case the bromine salt having the higher Néel temperature.

[6] W. K. Robinson and S. A. Friedberg, Bull. Am. Phys. Soc. Ser. II, 4, 183 (1959).

[7] Spence, Forstat, Khan, and Taylor, J. Chem. Phys. **31**, 555 (1959).

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Spin Alignment in the Superconducting State

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It is argued that spin alignment can and will occur for ion-core spins in superconductors, but that the alignment is in the form of extremely small domains. Central to the argument is the concept of the nonlocal susceptibility $\chi(r-r')$, which leads to a positive short-range Kittel-Ruderman-Yosida interaction of ion-core spins, but a negative long-range interaction of range ξ_0.

Very general arguments suggest that purely ferromagnetic alignment should not be observed in preference to this domain-like "cryptoferromagnetic" alignment.

SPECIFIC heat data on a 0.7% Gd in La sample[1] indicate an alignment of Gd spins in the superconducting state. An almost equally convincing demonstration of such alignment is the observation in (Ce-Gd)Ru_2 that the superconducting transition can occur below a ferromagnetic one,[2] although the ferromagnetic energy per atom, $\sim kT_c(N_I/N)\ln(2S+1)$, must be $\sim$100 times the superconducting energy $\sim kT_c(kT_c/\epsilon_F)$ (since the entropy in the ferromagnetic transition is far larger); some alignment must lower the energy of the superconducting state correspondingly.

It is here suggested that this alignment occurs and is ferromagnetic, but only in extremely small domains, certainly smaller than the coherence length ξ_0 and probably of the order $(r_s{}^2\xi_0)$—about $(50\text{ A})^3$. The domains may even be so small that density fluctuations (or the absence of true long-range order) account for the transition breadth. The net polarization averaged over the coherence length must, by very general arguments, be nearly zero.

To see these facts, we start by understanding the general phenomenon of spin-coupling via polarization of conduction electrons. We write the exchange interaction of rare earth ion spins $\mathbf{S}_j$ and conduction-electron spin density $\mathbf{s}(\mathbf{r})$[3]:

$$H'=\Omega_0\sum_j\int d\tau\, J(|\mathbf{r}-\mathbf{R}_j|)\mathbf{s}(\mathbf{r})\cdot\mathbf{S}_j, \qquad (1)$$

J being the exchange integral, the r-dependence of which will serve only as a short-wave cutoff; Ω_0 is the cell volume.

The conduction-electron spin polarization resulting from this interaction is given by a position-dependent susceptibility $\chi(r)$:

$$\mathbf{s}(\mathbf{r})=J\sum_j\chi(|\mathbf{r}-\mathbf{R}_j|)\mathbf{S}_j, \qquad (2)$$

resulting from the action of the "effective field" $J\mathbf{S}_j$ on the electron gas, which responds according to its susceptibility. This spin density reacts back on the ion cores, resulting in the spin polarization energy

$$U=-\tfrac{1}{2}J^2\sum_{j,j'}\chi(|\mathbf{R}_j-\mathbf{R}_{j'}|)\mathbf{S}_j\cdot\mathbf{S}_{j'} \qquad (3)$$

$$=-\tfrac{1}{2}J^2\sum_{\mathbf{q}}\chi(q)|\mathbf{S}(\mathbf{q})|^2, \qquad (4)$$

where

$$\mathbf{S}(\mathbf{q})=(1/\sqrt{N})\sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j}\mathbf{S}_j,$$

$$\chi(q)=(1/\Omega)\int d\tau\,\chi(R)e^{-i\mathbf{q}\cdot\mathbf{R}}. \qquad (5)$$

We have introduced here the wave-number-dependent susceptibility, $\chi(q)$, which determines the interaction with a spin density of wave number q. $\chi(q=0)$ is the usual Pauli spin susceptibility. The difference from the normal state of the integral of (3) or (4) for a paramagnetic arrangement of $\mathbf{S}_j$'s was the result found in Suhl and Matthias,[3] giving the loss in energy of the superconducting state.

In the normal metal, $\chi(|\mathbf{r}-\mathbf{r}'|)$ is like the Ruderman-

[1] N. Phillips (to be published).

[2] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 449 (1958).

[3] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1959); Phys. Rev. Letters **2**, 5 (1958); Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 93 (1958).

Kittel result,[4] finite and positive on the average at short range [its average is $\chi(q=0)$] but falling to zero at large distances.[5] In the superconductor, $\chi(q=0)$ is zero if the B.C.S. (Bardeen-Cooper-Schrieffer) theory is right,[6] and is experimentally observed to be much reduced.[7] Since the short-range interaction cannot be much changed, there must be a negative long-range contribution; we shall see that its range is the coherence length ξ_0. This makes the situation closely similar to that which forms domains in ferromagnets: the parallel short-range interaction is satisfied by parallel ordering locally, while the negative long-range force is made ineffective by the formation of domains, at little cost in short-range energy.

To obtain a quantitative estimate of domain size we calculate the two contributions to χ. The short-range one is the usual Kittel-Ruderman interaction,[4] given as a function of wave number by Yosida[5]:

$$\chi(q)=\chi(q=0)(\tfrac{1}{2})\left[1+(4k_F{}^2-q^2)(4k_Fq)^{-1}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right]$$
$$\simeq\chi(q=0)\left(1-\frac{q^2}{12k_F{}^2}+\cdots\right), \quad (6)$$

the latter for long wavelengths. The long-range part of the force results from the difference of superconducting and normal susceptibilities, which we calculate[6] to be

$$\Delta\chi(r)=\chi_N(r)-\chi_S(r)$$
$$=|N(0)|^2\int d\mathbf{k}\int d\mathbf{q}\, e^{i\mathbf{q}\cdot\mathbf{r}}$$
$$\times\left[L(\epsilon_k,\epsilon_{k+q})-\frac{f(\epsilon_{k+q})-f(\epsilon_k)}{\epsilon_k-\epsilon_{k+q}}\right]. \quad (7)$$

This may be expressed over most of the relevant range in terms of the nonlocal kernel function $J(R,0)$ evaluated by B.C.S., which has as its range the coherence length ξ_0:

$$\Delta\chi(R)/\Delta\chi(0)=J(R,0)k_F{}^{-2}R^{-2}. \quad (8)$$

In momentum space $\Delta\chi(q)$ is related to the $K(q)$ integral[6]; we have not evaluated it exactly but in the relevant range

$$\Delta\chi(q)=\Delta\chi(0)(\pi/2\xi_0q). \quad (9)$$

χ as a function of q is shown schematically in Fig. 1 for normal and superconducting cases.

The domain pattern will be characterized by a wave number q_d, giving the inverse size of its structure, which

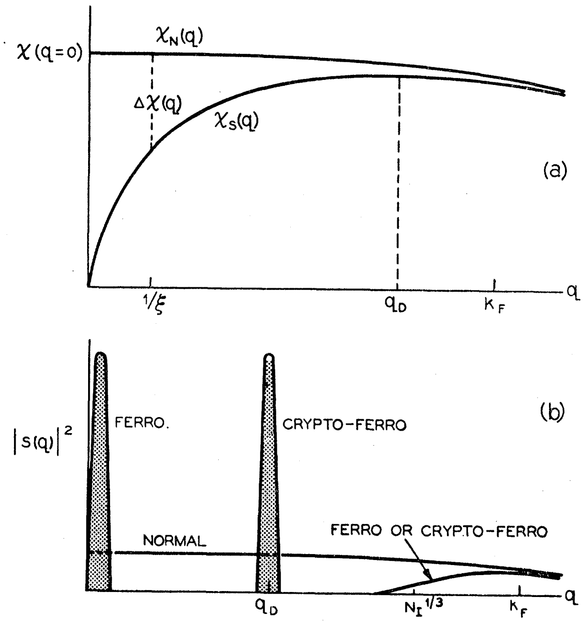

FIG. 1. (a) $\chi(q)$ in normal and superconducting states. (b) $|S(q)|^2$ in paramagnetic, ferromagnetic, and cryptoferromagnetic states.

must be close to the wave number of maximum $\chi_S(q)$. (See Fig. 1.) Maximizing χ_S by use of (6) and (9), we obtain

$$q_d=(3\pi k_F{}^2\xi_0{}^{-1})^{\frac{1}{3}},\qquad \lambda_d\simeq 50\text{ A}, \quad (10)$$

and

$$\Delta\chi=\chi(q=0)\times\tfrac{1}{4}(3\pi/k_F\xi_0)^{\frac{2}{3}}\simeq 2\times10^{-3}\Delta\chi(q=0). \quad (11)$$

In order of magnitude the ferromagnetic energy is $(N_I/N)(\epsilon_F/\epsilon_0)\simeq 100$ times the superconducting energy, so that the energy of the superconducting state with this "cryptoferromagnetic" alignment is slightly lower than the true ferromagnetic state and alignment is expected to occur. Note that large anisotropy may change these conclusions quantitatively.

So far we have assumed that the wave function of the superconducting state is unchanged by the alignment, so we have calculated an upper limit on the energy of the cryptoferromagnetic state. Actually, the superconducting state may adjust itself so as to improve matters considerably. To see this, return to the expression (4). In the paramagnetic state, there is no correlation among the $\mathbf{S}_j$'s, so that $\langle|\mathbf{S}(\mathbf{q})|^2\rangle$ is a constant, $S(S+1)(N_I/N)$.

Now there is a sum rule for the $\mathbf{S}(\mathbf{q})$'s,

$$\sum_j \mathbf{S}_j{}^2=\sum_q|\mathbf{S}(\mathbf{q})|^2=N_IS(S+1). \quad (12)$$

When ferromagnetic or cryptoferromagnetic alignment is present, one particular $\mathbf{S}(\mathbf{q})$ takes on a very large value,

$$S(q_d)\cong SN_I/\sqrt{N},$$

[4] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

[5] K. Yosida, Phys. Rev. **106**, 893 (1957).

[6] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). But see R. Ferrell, Phys. Rev. Letters **3**, 262 (1959); P. W. Anderson, Phys. Rev. Letters **3**, 325 (1959) for a mechanism whereby $\chi(0)$ may be considerably increased. As emphasized later, such an increase does not modify these results seriously.

[7] F. Reif, Phys. Rev. **106**, 208 (1957); G. M. Androes and W. D. Knight, Phys. Rev. Letters **2**, 386 (1959).

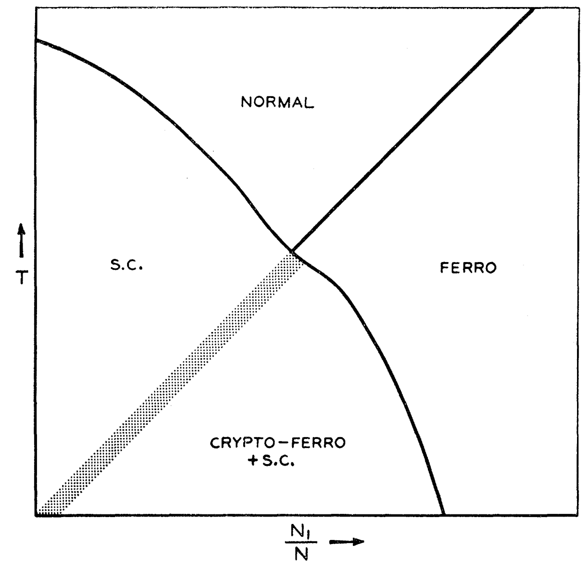

FIG. 2. Phase diagram for ferromagnetism, superconductivity, and cryptoferromagnetism.

so that

$$\sum_{\mathbf{q}\neq\mathbf{q}_d} |\mathbf{S}(\mathbf{q})|^2=(N_I/N)\left[S+S^2\left(1-\frac{N_I}{N}\right)\right]. \quad (13)$$

That is, the random magnetic scattering is reduced in proportion to N_I/N and replaced by a spin-dependent periodic potential of wavelength λ_d. This situation is shown in the second half of Fig. 1.

One can show that the energy of the superconducting cryptoferromagnetic state may possibly be lowered relative to that of the superconducting, normal state by an additional amount $(N_I/N)^{\frac{2}{3}}$ times the Herring-Suhl-Matthias[3] scattering effect, so that the superconducting transition in the aligned state may actually be slightly higher than in the paramagnetic state. Figure 2 shows schematically the type of phase diagram which might be expected to result from the above considerations.

A final remark is that these considerations do not depend seriously on the special features of the B.C.S. theory, but only upon a reduction, for superconductors, in the long-wavelength paramagnetic susceptibility (not necessarily to zero). In particular, we can conclude that a long-range purely ferromagnetic alignment in a superconductor cannot occur unless (a) the paramagnetic susceptibility of the superconductor is not reduced, contradicting the experimental and theoretical results; or (b) the exchange interaction of conduction electrons and ionic spins is inexplicably small; otherwise the ferromagnetic normal state is necessarily far lower in energy than the superconductor. Unfortunately, present experiments indicate such alignment in some cases.[8]

ACKNOWLEDGMENTS

We would like to thank T. H. Geballe, B. T. Matthias, and N. Phillips for calling our attention to their unpublished work.

[8] B. T. Matthias (private communication) shows that homogeneous superconducting samples exhibit a ferromagnetic moment, but it is not clear to what extent the observed remanence is affected by trapped flux.

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Initial Estimates for Self-Consistent Field Calculations for Atoms with Large Atomic Number

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Absolute rather than interpolation methods are described for obtaining initial estimates for self-consistent field calculations with exchange. Tables have been computed so that the procedure is entirely numerical which makes it more convenient than Hartree's graphic interpolation scheme.

INTRODUCTION

SELF-CONSISTENT field calculations with exchange require initial estimates of the following three quantities: (i) the radial wave functions, $P(nl;r)$, (ii) $a_0=P(nl;r)/r^{l+1}$, for $r\rightarrow 0$, and (iii) the energy parameter $\epsilon_{nl,nl}$. In this paper methods will be described for estimating these quantities when the atomic number N is large; they all depend on knowing the limiting behavior of the estimate as $N\rightarrow\infty$.

Previous papers[1,2] showed that if we represent the wave functions by a series in $1/N$ so that

$$N^{-\frac{1}{2}}P(nl;r)=P_H(nl;\rho)+[Q(nl;\rho)/N]+[R(nl;\rho)/N^2]+\cdots,\quad \rho=Nr, \quad (1)$$

and if we assume that

$$\epsilon_{nl,nl}=(1/n^2)+(\epsilon_1/N)+(\epsilon_2/N^2)+\cdots, \quad (2)$$

[1] C. Froese, Proc. Roy. Soc. (London) **A239**, 311 (1957).
[2] C. Froese, Proc. Roy. Soc. (London) **A244**, 390 (1958).