

where  $\beta = N(K, \epsilon) |F|$ . The binding energy,  $\Delta$ , is independent of the volume of the box, but is strongly dependent on the parameter  $\beta$ .

Following a method of Bardeen,<sup>5</sup> by which the coupling constant for the electron-electron interaction, which is due to phonon exchange, is related to the high-temperature resistivity which is due to phonon absorption, one gets  $\beta \simeq \rho n \times 10^{-6}$ , where  $\rho$  is the high-temperature resistivity in esu and  $n$  is the number of valence electrons per unit volume. The binding energy displays a sharp change of behavior in the region  $\beta \simeq 1$  and it is just this region which separates, in almost every case, the superconducting from the nonsuperconducting metals.<sup>5</sup> (Also it is just in this region where the attractive interaction between electrons, due to the phonon field, becomes about equal to the screened Coulomb repulsive interaction.)

The ground-state wave function,

$$\chi_0(\mathbf{r}, K) = (\text{const}) \int \frac{e^{i\mathbf{k} \cdot \mathbf{r}} N(K, \epsilon(\mathbf{k}))}{\mathcal{E}_K + \epsilon(\mathbf{k}) - E} \left( \frac{d\epsilon}{dk} \right) d\mathbf{k}, \quad (6)$$

represents a true bound state which for large values of  $r$  decreases at least as rapidly as  $\text{const}/r^2$ . The average extension of the pair,  $[\langle r^2 \rangle_{\chi_0}]^{1/2}$ , is of the order of  $10^{-4}$  cm for  $\Delta \simeq kT_c$ . The existence of such a bound state with nonexponential dependence for large  $r$  is due to the exclusion of the states  $k < k_0$  from the unperturbed spectrum, and the concomitant degeneracy of the lowest energy states of the unperturbed system. One would get no such state if the potential between the electrons were always repulsive. All of the excited states  $\chi_{n>0}(\mathbf{r}, K)$  are very nearly plane waves.

The pair described by  $\chi_0(\mathbf{r})$  may be thought to have some Bose properties (to the extent that the binding energy of the pair is larger than the energy of interaction between pairs).<sup>6</sup> However, since  $N(K, \epsilon)$  is strongly dependent on the total momentum of the pair,  $K$ , the binding energy  $\Delta$  is a very sensitive function of  $K$ , being a maximum where  $K=0$  and going very rapidly to zero where  $K \simeq k_m - k_0$ . Thus the elementary excitations of the pair might correspond to the splitting of the pair rather than to increasing the kinetic energy of the pair.

In either case the density of excited states ( $dN/dE$ ) would be greatly reduced from the free-particle density and the elementary excitations would be removed from the ground state by what amounted to a small energy gap.

If the many-body system could be considered (at least to a lowest approximation) a collection of pairs of this kind above a Fermi sea, we would have (whether or not the pairs had significant Bose properties) a model similar to that proposed by Bardeen which would display many of the equilibrium properties of the superconducting state.

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<sup>2</sup> See also, for further references and a general review, J. Bardeen, *Theory of Superconductivity Handbuch der Physik* (Springer-Verlag, Berlin, to be published), Vol. 15, p. 274.

<sup>3</sup> J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

<sup>4</sup> H. Fröhlich, Proc. Roy. Soc. (London) **A215**, 291 (1952).

<sup>5</sup> John Bardeen, Phys. Rev. **80**, 567 (1950).

<sup>6</sup> It has also been suggested that superconducting properties would result if electrons could combine in even groupings so that the resulting aggregates would obey Bose statistics. V. L. Ginzburg, Uspekhi Fiz. Nauk **48**, 25 (1952); M. R. Schafroth, Phys. Rev. **100**, 463 (1955).

## Magnetic Resonance in Manganese Fluoride

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NUCLEAR magnetic resonance of the fluorine nuclei in  $\text{MnF}_2$  has recently been observed by Shulman and Jaccarino,<sup>1</sup> who found a much greater "paramagnetic shift" of the resonance field than would be expected from simple magnetic dipole fields of the manganese ions. Electronic paramagnetic resonance of  $\text{Mn}^{2+}$  ions present as impurities in the isomorphous crystal  $\text{ZnF}_2$  has previously been observed by Tinkham,<sup>2</sup> who made detailed measurements of the fluorine hyperfine structure which results from overlap of the magnetic electrons onto the fluorine ions. The purpose of this note is to point out that the shift of the nuclear resonance can be estimated from Tinkham's data, and that good agreement with the measured value is found.

With an obvious extension of Tinkham's nomenclature, the Hamiltonian for the system can be written as

$$\mathcal{H} = -g_N \beta_N \mathbf{H} \cdot \mathbf{I} + \sum_N \mathbf{I} \cdot A^N \cdot \mathbf{S}^N, \quad (1)$$

where  $\mathbf{I}$  is the spin operator for a fluorine nucleus,  $A^N$  is the hyperfine structure constant for interaction between this nucleus and the  $N$ th manganese ion whose spin operator is  $\mathbf{S}^N$ . Owing to the rapid change of spin orientation for the manganese ions, we must take a weighted mean of the different values of the projection  $M$  of  $\mathbf{S}^N$  on the direction of the applied field. This mean is

$$\bar{M} = \sum_M M \exp(-W_M/kT) / \sum_M \exp(-W_M/kT),$$

which cannot be evaluated from first principles in a substance such as  $\text{MnF}_2$  where strong internal fields are acting. However, we may relate it to the measured susceptibility, since, per mole,

$$\chi = N g \beta \bar{M} / H.$$

Hence we have, for the quantum of energy required to

reverse the fluorine spin,

$$\begin{aligned} h\nu &= g_N \beta_N H - \bar{M} \Sigma A^N \\ &= g_N \beta_N H - (\chi H / N g \beta) \Sigma A^N \\ &= g_N \beta_N H (1 - \alpha), \end{aligned} \quad (2)$$

where

$$\begin{aligned} \alpha &= (\chi / N g \beta g_N \beta_N) \Sigma A^N \\ &= 669 \chi \Sigma A^N, \end{aligned} \quad (3)$$

if  $A$  is in units of  $\text{cm}^{-1}$ .

Each  $A$  is an anisotropic tensor quantity, whose value for a direction  $(l, m, n)$  with respect to its principal axes is given by

$$A^2 = l^2 A_x^2 + m^2 A_y^2 + n^2 A_z^2.$$

Thus in an arbitrary plane the shift, if small, should vary with  $\cos^2\theta$ , where  $\theta$  is the angle between the external magnetic field and one of the directions of maximum shift in this plane, as shown in Fig. 2 of reference 1. Each fluorine is bonded to three nearest  $\text{Mn}^{2+}$  ions, and if bonding to other ions is neglected, it can be shown that the extreme values of  $\Sigma A^N$  in the  $ab$ -plane are  $(2A_y^I + A_x^{II})$  and  $(2A_x^I + A_y^{II})$  respectively (the nomenclature is that of reference 2). In Tinkham's experiments  $A_x$  could not be determined owing to lack of resolution, but the values for the other directions are

$$\left. \begin{aligned} A_y^I &= 16.5 \pm 0.7, & A_y^{II} &= 14.6 \pm 1.2 \\ A_x^I &= 18.2 \pm 0.2, & A_x^{II} &= 12.5 \pm 0.2 \end{aligned} \right\} \times 10^{-4} \text{ cm}^{-1},$$

and he estimates that  $A_x^I$  is nearly equal to  $A_y^I$ , while  $A_x^{II}$  is nearly 30% larger than  $A_y^{II}$ . This gives a mean value in the  $ab$ -plane of  $\Sigma A^N = A_x^I + A_y^I + \frac{1}{2} A_x^{II} + \frac{1}{2} A_y^{II} = (49.5 \pm 4) \times 10^{-4} \text{ cm}^{-1}$ . With the susceptibility data of de Haas, Schultz, and Koolhaas,<sup>3</sup> this gives at 77°K the value  $\alpha = 0.077 \pm 0.006$ , in close agreement with the observed value 0.0776 (with demagnetizing correction). The exact agreement is fortuitous, since Tinkham's estimates give too small an anisotropy for the shift in the  $ab$ -plane. A more delicate test would be obtained from a measurement along the  $c$ -axis ( $z$ -axis) where Tinkham's results are more precise [ $2A_x^I + A_x^{II} = (48.9 \pm 0.6) \times 10^{-4} \text{ cm}^{-1}$ ; giving  $\alpha = 0.0759 \pm 0.001$  at 77°K].

Shulman and Jaccarino report that the fluorine resonance disappears in the antiferromagnetic state. If the manganese ions are then in their states  $M_z = \pm 5/2$ , there will be a large field at the fluorine nucleus parallel to the  $c$ -axis even in the absence of an external field. Since the two type I manganese ions to which the fluorine is bonded belong to one sublattice, while the type II manganese belongs to the other sublattice, the resonance should occur at  $h\nu = (5/2)(2A_x^I - A_x^{II})$ , or at a frequency of  $179 \pm 2 \text{ Mc/sec}$ . With an oscillatory field normal to the  $c$ -axis, it may be possible to detect this resonance at low temperatures, but  $A^N$  is sensitive to

small changes in the bond distances and the frequency may be slightly different from that computed above by using Tinkham's data on  $\text{Mn}^{2+}$  ions in  $\text{ZnF}_2$ .

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## Thiourea, a New Ferroelectric

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THIOUREA is orthorhombic at room temperature.<sup>1</sup> When evaporated silver electrodes are applied to (010) faces of thin, clear plates, hysteresis loops are observed below  $-104.8^\circ\text{C}$  and a pronounced dielectric constant anomaly is found in this neighborhood. Immediately above this temperature, double loops similar to those described for  $\text{BaTiO}_3$ <sup>2</sup> are observed. The spontaneous polarization is approximately 3.1 microcoulombs/cm<sup>2</sup> and the coercive field is less than 1000 volts/cm at 60 cycles and  $-110^\circ\text{C}$ .

Clear crystals have been obtained by the slow evaporation of a saturated solution of thiourea (Distillation Products Industries) in methanol. By slow growth with stirring in a bath held around  $30^\circ\text{C}$ , thin tablets were grown with (010) faces which were electrodeposited following an alcohol wash. Some solutions yielded small, clear hexagonal-based prisms which could be cleaved perpendicular to the ferroelectric direction into thin plates.

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## Simulation of Solar Prominence in the Laboratory\*

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IT is possible to locate a source<sup>1</sup> of plasma in the pole piece of a horseshoe (permanent) magnet, as shown in Fig. 1, and project the plasma outward along the lines of magnetic force. If only one plasma source is employed and the magnet and the vacuum tank "float"