Observation of antiferromagnetic resonance in the DPPH free radical

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An antiferromagnetic-resonance signal has been observed in the DPPH free radical at temperatures below 0.76 K. A "spin-flop" phase exists in this system. A magnetic state diagram is constructed.

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The DPPH (α, α_1-diphenyl-β-picrylhydrazyl) free radical is a paramagnetic substance which has been studied extensively by electron spin resonance (ESR). Prokhorov *et al.*[1] found that the resonance signal vanishes at very low temperatures and attributed this effect to a phase transition of the radical to an antiferromagnetic state. Further study[2] has shown that the transition temperature is very sensitive to the particular solvent from which the radical is crystallized. When the DPPH radical is crystallized from benzene, for example, the transition temperature is 0.25 K, while for a concentrated sample it is ~1 K. Although DPPH in the paramagnetic state has been the subject of many studies, no direct study of the ordered phase has thus far been found possible. In this letter we are reporting the observation of an antiferromagnetic resonance and the first results of a study of the magnetic phase diagram of this system.

The present experiments were carried out with polycrystalline samples of the DPPH radical crystallized from a hexane-pyridine mixture. The concentration of the radical approached 100% according to chemical analysis. The transition temperature was ~0.9 K according to ESR measurements. A resonance in the ordered phase was sought on an rf spectrometer with a working frequency of 300 MHz in a ^{3}He cryostat. A constant magnetic field of up to 8 kOe, homogeneous within $\sim 10^{-4}$, was produced by a standard electromagnetic.

A weak resonance signal from the ordered phase was observed at low temperatures in a magnetic field $H_0 = 1125 \pm 15$ Oe; within the experimental errors, this field was independent of the temperature (Fig. 1). As the temperature was raised, the resonance signal weakened slightly, and it disappeared at $T = 0.76 \pm 0.01$ K.

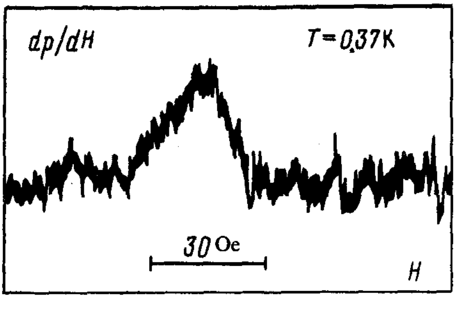

FIG. 1. The antiferromagnetic-resonance signal at $T = 0.38$ K.

Since the temperature at which this system undergoes the transition of the ordered state is very low, so that the exchange field is weak, and since we know that this system can be described well by the isotropic Heisenberg model, it may be suggested that the sublattice flop field is lower than H_0.

The magnetic susceptibility was measured in order to construct a phase diagram. These measurements were based on the change in the frequency of a tunnel-diode autodyne oscillator with a working frequency of 354 kHz as a function of the susceptibility of the sample. The resonance coil with the sample was placed in a ^{3}He bath, and the tunnel diode was held at a constant temperature $T = 1.4$ K in a ^{4}He bath. The constant magnetic field of up to ~ 20 kOe in these measurements was produced by a small superconducting solenoid around the ^{3}He bath. As usual, the temperature of the antiferromagnetic transition was determined for various values of the external magnetic field, $T_c(H)$, from the characteristic slope change on the experimental temperature dependence of the susceptibility of the sample.[3] The results of these measurements are in quantitative agreement with the data obtained from the disappearance of the ESR signal. Figure 2 shows a typical plot of χ against the applied magnetic field at $T < T_c$. This experimental $\chi(H)$ dependence is distorted by a monotonic shift of the autodyne frequency upon an increase of the magnetic field in the solenoid. This parasitic shift has a negligible effect on the accuracy with which the critical fields H_{c1} and H_{c2} are determined. A phase diagram (Fig. 3) was plotted from the values of the critical fields and the measured values of $T_c(H)$. The resulting diagram has a shape typical of simple two-sublattice antiferromagnets with a bicritical point.[3,4]

According to the resulting state diagram, the antiferromagnetic resonance observed at temperatures $T < 0.76$ K in the magnetic field $H_0 \approx 1125$ Oe should be assigned to a "spin-flop" phase. Since the resonant frequency and the flop field are both nearly totally independent of the temperature, it may be suggested that the parameters governing these properties have reached saturation. If so, the equations which hold for a zero temperature can be used. The resonant frequency is described satisfactorily by the expression for an antiferromagnet with a uniaxial anisotropy with a parallel orientation of the external magnetic field[5]:

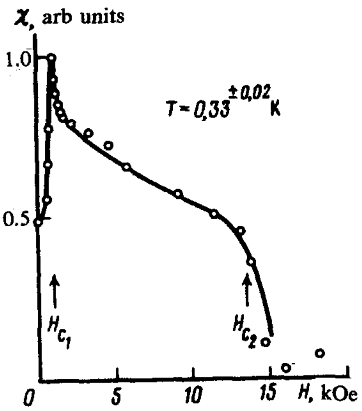

FIG. 2. Dependence of the susceptibility of DPPH in the ordered phase on the magnetic field. H_{c1}—Sublattice-flop field; H_{c2}—sublattice-collapse field.

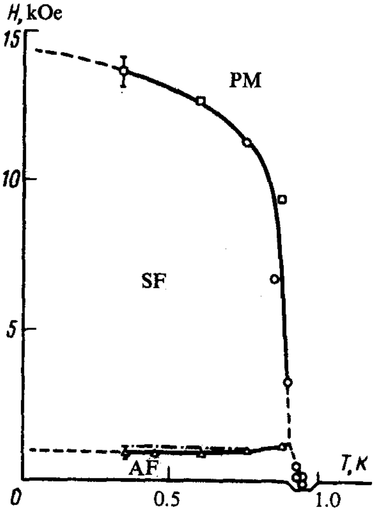

FIG. 3. Magnetic phase diagram. AF—Antiferromagnetic phase; SF—spin-flop phase; PM—paramagnetic phase. Δ, □—experimental critical fields determined from the measurements of $\chi(H)$; ○—transition temperatures found from the $\chi(T)$ dependence at various values of H; dot-dashed line—the resonant field.

$$(\omega/\gamma)^2 \approx H_0^2 - 2H_E H_A, \tag{1}$$

where ω is the resonant frequency, γ is the gyromagnetic ratio, H_0 is the applied field, H_E is the exchange field, and H_A is the anistropy field.[1] The parameters H_A and H_E in (1) are related to the fields H_{c1} and H_{c2}, which can be determined experimentally, by the familiar expressions $H_{c1} \approx \sqrt{2H_E H_A}$, and $H_{c2} \approx 2H_E$ at $T = 0$. Expression (1) holds within the error of the measurement of the critical fields. Most of the error stems from the inhomogeneity of the field of the superconducting solenoid in the volume of the sample. Expression (1) holds for an antiferromagnetic single crystal, while the sample in the present experiments is a fine-grain powder. It should thus be concluded that the resonance signal is built up exclusively by signals from grains whose anisotropy axes are approximately parallel to the external field. This assumption agrees with the low intensity of the resonance signal. The dot-dashed line in Fig. 3 shows the resonant field. As the temperature is raised, this line intersects the boundary of the spin-flop phase at $T = 0.76$ K. We wish to emphasize that the antiferromagnetic-resonance signal disappears at this temperature.

From these experimental results we can find the coordinates of the bicritical point on the phase diagram: $T_{bc} = 0.91 \pm 0.02$ K, $H_{bc} = 1270 \pm 150$ Oe. Finally, we note that an extrapolation of the phase boundaries to the region of the bicritical point (as illustrated by dashed lines in Fig. 3) leads to results in agreement with a quadratic magnetic-field dependence of the transition temperature, as predicted by the theory of Refs. 3 and 6.

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[1] Furthermore, among all possible types of anisotropy and all possible orientations of the external magnetic field with respect to the antiferromagnetism axis, only relation (1) corresponds to the resonant conditions of the present experiments. This circumstance provides independent confirmation of the existence of a spin-flop phase in this case.

[1]A. M. Prokhorov and V. B. Fedorov, Zh. Eksp. Teor. Fiz. **43**, 2105 (1962) [Sov. Phys. JETP **16**, 1489 (1963)].
[2]A. P. Kessel', B. M. Kozyrev, É. G. Kharakhash'yan, S. Ya. Khlebnikov, and Sh. Z. Shakirov, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 649 (1973) [JETP Lett. **17**, 453 (1973)].
[3]A. S. Borovik-Romanov, "Antiferromagnetism," in: Itogi nauki, Fiz.-mat. nauki (Scientific Progress; Division of Physical and Mathematical Sciences), No. 4, Izd. Akad. Nauk SSR, 1962.
[4]M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. **32**, 1350 (1974).
[5]A. G. Gurevich, Magnitnyĭ rezonans v ferritakh i antiferromagnetikakh (Magnetic Resonances in Ferrites and Antiferromagnets), Nauka, Moscow, 1973.
[6]A. Z. Patashinskiĭ, V. L. Pokrovskiĭ, and S. B. Khokhlachev, Zh. Eksp.Teor.Fiz. **63**, 1521 (1972) [Sov. Phys. JETP **36**, 807 (1973)].

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