SOVIET PHYSICS JETP VOLUME 20, NUMBER 5 MAY, 1965

ANTIFERROMAGNETISM OF DIBENZENE CHROMIUM IODIDE

Yu. S. KARIMOV and I. F. SHCHEGOLEV

Institute for Physics Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor June 17, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 47, 1721-1726 (November, 1964)

Antiferromagnetic ordering was observed in dibenzene chromium iodide at temperatures below 0.75°K. The proton magnetic resonance in the antiferromagnetic state was studied in a zero external magnetic field. The magnetic structure of the ordered state is discussed.

INTRODUCTION

THE problem of the transition of organic paramagnets into a magnetically ordered state has been discussed for some time. The majority of the investigated crystalline free radicals have a narrow electron paramagnetic resonance line, indicating considerable exchange interactions between unpaired electrons. On the other hand, investigation of the magnetic properties of organic paramagnets in the temperature range from 78 to 295°K have shown that the magnetic susceptibility of many of them obeys the Curie-Weiss law with a very high characteristic temperature (for example, up to 50° K [1]). Therefore, we may assume that, at least at liquid helium temperatures, some of the organic paramagnets are in a magnetically ordered state.

Investigations at lower temperatures have shown, however, that although organic paramagnets do possess very unusual magnetic properties,[2] they do not exhibit the magnetic ordering characteristic of inorganic paramagnets. McConnell and Lynden-Bell [3] have shown that the reason for this behavior is the fact that in the majority of cases, organic paramagnetic crystals consist of large and relatively asymmetric molecules. In such crystals, each of the molecules may interact strongly only with one or two nearest neighbors. Therefore, interacting molecules form pairs or linear chains. This model, at least qualitatively, explains all the anomalies observed in the magnetic susceptibility.[4]

Organic paramagnets, to which the above remarks do not apply, are compounds of the sandwich type, where every molecule interacts equally strongly with more than two neighbors. It has been discovered [5] that paramagnetic iodides of dibenzene chromium and ditoluene chromium have anomalous magnetic properties at very low temperatures. The present work reports a detailed study of the behavior of dibenzene chromium iodide and shows that at 0.75°K this compound goes over into the antiferromagnetic state.

RESULTS

The apparatus used to investigate the nuclear and electron resonance in the temperature range from 0.08 to 1.5° K differed from that described in [5] in one respect only: the tested polycrystalline sample was placed in the apparatus in the form of a bar, into which the branched end of a copper heat conductor was inserted. The other end of this conductor was, as usual, connected to a pellet of iron-alumina alum. This made it possible to increase the space factor of the oscillator coil and improve the thermal contact between the alum salt and the sample.

As mentioned above,[5] at 0.75° K the proton resonance signal disappears suddenly. The shift of the center of gravity of the absorption line and its width do not exhibit any anomalies up to the temperature at which the signal disappears. This is to be expected because both these quantities are proportional to the magnetic susceptibility.[6] It is interesting that when disappearing the line does not broaden gradually but only its intensity changes. This is associated with the fact that the main contribution to the absorption line width is made by the anisotropic dipole interaction.[6] The temperature interval in which the line disappears (its intensity changes from 0.9 to 0.1) amounts to about 0.05 deg.

In the earlier paper [5], we also reported that the electron paramagnetic resonance line did not disappear at temperatures below 0.75° K, where the proton resonance signal was no longer observed. A careful study showed, however, that the electron resonance signal observed below

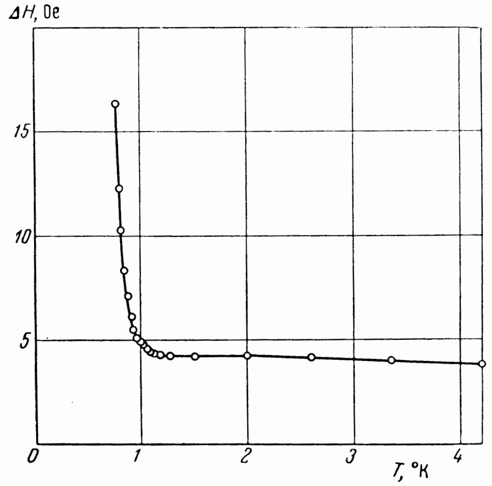

FIG. 1. Temperature dependence of the electron resonance line width.

0.75° K was due to the presence of diamagnetic and paramagnetic impurities in the sample. The dependence of the electron resonance line width on temperature for purer samples is shown in Fig. 1.

The measurements were carried out at a frequency of 80 Mc, the line width being determined as the separation between the maximum values of the derivative of the absorption line. The signal intensity in the temperature range from 0.8 to 4.2°K varied in accordance with the Curie-Weiss law $1 \propto (T - \Theta)^{-1}$, where the value of Θ was identical within the experimental error, with the value obtained from measurements of the static susceptibility ($\Theta = -4.6°$).[6] At 0.75° K, the electron resonance line broadened so much that it could hardly be measured; below this temperature the signal was absent.

In our earlier work, an attempt was made to detect the proton resonance line in a zero external magnetic field below 0.75°K.[5] In these experiments, the frequency of the threshold oscillator remained constant and the resonance was obtained by varying the sample temperature. We were unable to detect the resonance signal in this way. Therefore, we attempted to detect the proton resonance in a zero magnetic field by varying slightly the threshold oscillator frequency and employing frequency modulation.

The proton resonance frequency in a zero magnetic field at temperatures considerably below the transition temperature may be found from the formula

$$\nu = (gS\mu_B / h)\left[a + b(3\cos^2\vartheta - 1)\right], \qquad (1)$$

where g is the electron g-factor; S is the electron spin; μ_B is the Bohr magneton; h is Planck's constant; a and b are the isotropic and anisotropic constants of the hyperfine interaction; ϑ is the angle between the direction of the magnetic moment and the radius vector joining this moment with the nucleus considered. It is assumed in this formula that each proton interacts with only one magnetic moment. This is true, in the first approximation, in our case, where the internal molecular distances are much smaller than the distances between neighboring molecules.

The hyperfine interaction constants are known from experiments on the nuclear resonance in the paramagnetic region:[6] a = 3.15 Oe and b = 1.05 Oe. It follows from Eq. (1) that the proton resonance in a zero external magnetic field may be observed in the frequency range from 3 to 7.5 Mc. The exact value of the frequency depends on the magnetic moment's direction, in the ordered state, with respect to the crystallographic axes. For different directions of the magnetic moment, there will be different numbers of lines with different relative intensities, depending on the number of nonequivalent protons. The maximum number of lines, in our case, is four.

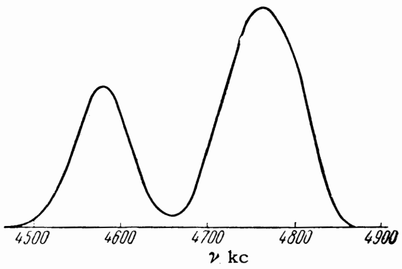

FIG. 2. Proton resonance absorption line in a zero field at T = 0.19° K.

We were able to detect the proton resonance signal in the range of frequencies mentioned above. Figure 2 shows a typical form of the absorption line obtained by double integration of the experimental curves. The absorption line was a fully resolved doublet with an intensity ratio 1 : 2 and the separation between its maxima equal to 185 ± 10 kc. The width, measured at half the amplitude, was 75 kc for the weaker and 105 kc for the stronger line. It is worth noting that the proton resonance signal in a zero external field below the transition temperature was about two orders of magnitude weaker than the signal in the paramagnetic region. The most probable reason for this behavior was the considerable increase in the spin-lattice relaxation time due to the transition of the sample to a magnetically ordered state, as a result of which the proton resonance signal could become considerably saturated. We were unable to verify this suggestion experimentally since our Pound-type threshold oscillator could not be used at too low amplitudes of the high-frequency field.

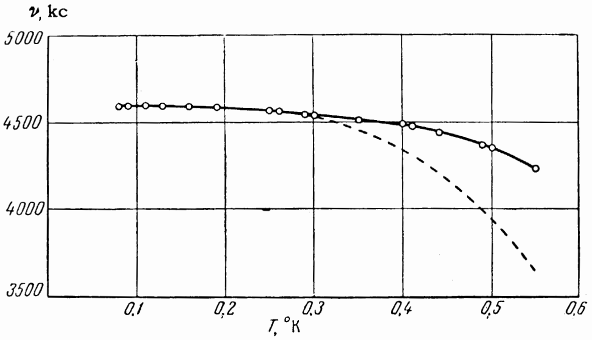

FIG. 3. Temperature dependence of the proton resonance frequency; the dashed curve shows the molecular field theory.

Figure 3 shows the temperature dependence of the proton resonance frequency in a zero external field, the frequency being that of the weaker absorption line. At 0.55°K, the line broadened by a factor of 2 and fell correspondingly in intensity. At higher temperatures, it was extremely difficult to observe the signal not only because of its weak intensity but also because of the strong temperature dependence of the resonance frequency. This explains the failure of previous attempts to detect this signal.[5]

DISCUSSION

Unfortunately, the crystallographic structure of dibenzene chromium iodide is unknown but for estimates we can use the data on the structure of ditoluene chromium iodide.[7] We shall assume that the lattice of dibenzene chromium iodide is simple cubic in the sense that the coordination number is 6 (Fig. 4a). The distance from the central chromium atom to the nearest iodine atoms will be assumed to be 6.27 Å, the distances Cr-C to be 2.08 Å, the distances C-C – 1.42 Å, and C-H, 1.8 Å. The unpaired electron in the dibenzene chromium iodide molecule is localized at the s-orbit of the chromium atom.[6]

All the experiments described here show that at 0.75° K dibenzene chromium iodide goes over into the antiferromagnetic state. The presence of the proton resonance signal in a zero external field is a particularly convincing proof of this. Analysis of the position and form of the proton resonance line yields information on the magnetic structure of dibenzene chromium iodide below the transition temperature.

The fact that the resonance line is a doublet indicates the presence of two nonequivalent proton groups in the molecule. Two nonequivalent proton positions may be obtained by directing the magnetic moment along the x or y axis, or along the equivalent directions in the xy plane (Fig. 4a).

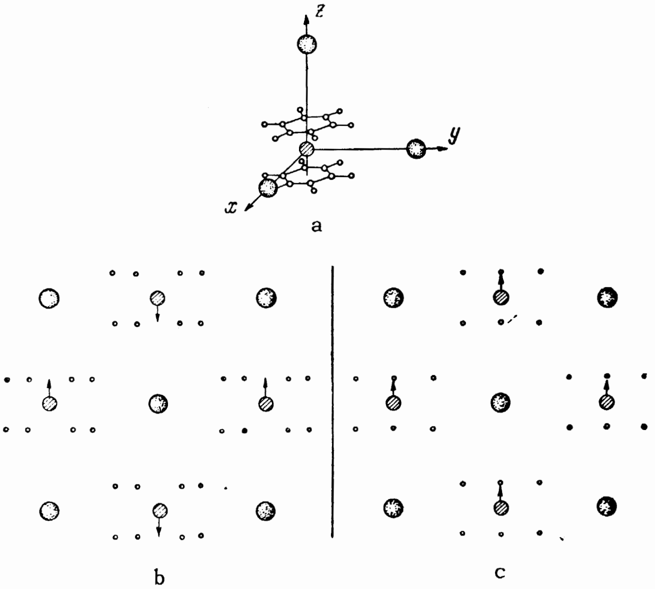

FIG. 4. a) Suggested crystal structure; b) and c) magnetic structure in the zy- and zx-planes, with carbon atoms omitted.

Such an orientation of the magnetic moment gives two absorption lines with the intensity ratio 1 : 2 but the distance between the lines for such a doublet, calculated using Eq. (1), is found to be an order of magnitude greater than the observed separation. The doublet is not obtained for any other direction of the magnetic moment. Therefore, it is natural to assume that the nonequivalence of protons is due to the influence of the magnetic moments of neighboring molecules. The best agreement between the observed and calculated values of the frequencies and intensities is obtained for the magnetic ordering shown in Figs. 4b and 4c.

If we disregard the influence of neighbors, the proton resonance signal should consist of a single line at 4.15 Mc, which is in fully satisfactory agreement with the observed resonance frequency value. If the dipole interaction with the magnetic moment of neighboring molecules is taken into account, the magnetic ordering shown in Figs. 4b and 4c gives rise to two proton resonance lines with the intensity ratio 1 : 2, the weaker line being at the lower frequencies and the distance between their maxima being about 260 kc.

The considerable difference between the calcu-

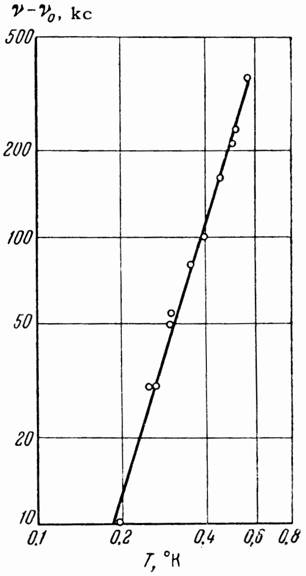

FIG. 5. Temperature dependence of the shift of the proton resonance frequency.

lated value of the splitting and the experimentally observed value (185 kc) is due to some difference between the real crystallographic structure of dibenzene chromium iodide and that shown in Fig. 4a. First, we may imagine that the lattice is slightly different from cubic and the distance along the y-axis to the nearest iodine atom is somewhat less than the distance along the x axis. It is sufficient to reduce the y-axis by 3% in order to account for the observed splitting. Second, the dibenzene chromium molecule may be rotated by a small angle about the z axis. Such a rotation also decreases the splitting between the lines. Moreover, it explains why the stronger line is much broader than the weaker line: a small rotation of the molecule about the z-axis makes the stronger line a poorly resolved doublet.

The nuclear resonance frequency in antiferromagnets is proportional to the sublattice magnetization (cf. for example,[8]). Because of this, there is considerable interest in the temperature dependence of the proton resonance frequency in a zero external field (Fig. 3). It is evident that the molecular-field theory gives, in our case, an unsatisfactory temperature dependence of the sublattice magnetization. In the whole investigated range of temperatures, the spontaneous magnetization decreases in accordance with the T^3 law, $(M_0 - M) \propto T^3$, which is illustrated in Fig. 5.

The authors express their profound gratitude to Academician P. L. Kapitza and A. S. Borovik-Romanov for their interest in this work and for their valuable comments. We are also grateful to V. M. Chibrikin for the supply of pure samples of dibenzene chromium iodide.

---

[1] W. Duffy, Jr., J. Chem. Phys. **36**, 490 (1962).

[2] Rhodes, Burgers, and Edelstein, Phys. Rev. Letters **6**, 462 (1961).

[3] H. M. McConnell and R. Lynden-Bell, J. Chem. Phys. **36**, 2393 (1962).

[4] A. S. Edelstein, J. Chem. Phys. **40**, 488 (1964).

[5] Yu. S. Karimov and I. F. Shchegolev, JETP **46**, 399 (1964), Soviet Phys. JETP **19**, 270 (1964).

[6] Karimov, Chibrikin, and Shchegolev, J. Phys. Chem. Solids **24**, 1683 (1963).

[7] O. V. Starovskiĭ and Yu. T. Struchkov, DAN SSSR **135**, 620 (1960).

[8] A. S. Borovik-Romanov, Itogi nauki, fiz.-mat. nauki, 4, Antiferromagnetizm (Progress in Sciences, Physico-Mathematical Sciences, 4, Antiferromagnetism), AN SSSR, 1962.

Translated by A. Tybulewicz
245