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EXPERIMENTAL VERIFICATION OF THE THERMODYNAMIC THEORY OF SPIN-SPIN PARAMAGNETIC RELAXATION IN PARALLEL FIELDS

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Paramagnetic spin-spin absorption has been investigated in a number of materials at ν = 600 Mcs at room temperature. It has been established that the absorption relation which follows from the Shaposhnikov analysis[1] is in good agreement with experiment if it is assumed that the corresponding relaxation time is independent of the constant field. The quantity b/c has been measured for certain materials for which it has been hitherto unknown.

1. The thermodynamic theory of paramagnetic relaxation in parallel fields[1] leads to the following expression for the imaginary part of the complex magnetic susceptibility

$$\chi''/\chi_0 m = F/\rho\nu + (1-F)^2 \rho_s \nu, \tag{1}$$

where χ_0 is the equilibrium specific susceptibility, m is the mass of the material being investigated, ρ is the spin-lattice relaxation time, ρ_s is the spin-spin relaxation time, ν is the frequency of the oscillating field, and F is a function of the constant field H_c, which will be discussed in detail below. The expression in (1) applies to the case in which $\rho_s \ll \rho$, $\rho_s\nu \ll 1$ and $\rho\nu \gg 1$. If the difference between ρ_s and ρ is large, by making the frequency ν high enough the first term in (1) becomes much smaller than the second. In this case the paramagnetic absorption is described by the relation

$$\chi''/\chi_0 m = (1-F)^2 \rho_s \nu \tag{2}$$

and can be discussed in terms of only one internal relaxation mechanism in the spin system.

Equation (2) has been checked by Garif'ianov[2] who has shown that it gives good agreement with experiment if it is assumed that ρ_s is independent of the constant field H_c. However, the sample in which this test was made was small. In Ref. 3 an investigation was made of spin-spin absorption in paramagnets in a much larger sample and it was established that in all cases considered the absorption takes place in accordance with Eq. (2) with ρ_s independent of H_c.

2. Assuming that ρ_s is independent of H_c, we write Eq. (2) in the form

$$\chi''(H_c) = (1-F)^2, \tag{3}$$

where $\chi''(H_c) \equiv \chi_0 m \rho_s \nu$. The readings in the grid circuit are proportional to the quantity $\chi'(H_c)$. The function F varies over the range $0 < F < 1$ when its argument H_c varies from zero to infinity since[4]

$$F = H_c^2 (b/c + H_c^2)^{-1}, \tag{4}$$

where b is the heat capacity of the spin system and c is the Curie constant (normal ferromagnets are being considered). From Eqs. (3) and (4) it follows that the spin-spin absorption $\chi''(H_c)$ is a decreasing function of H_c. Furthermore, when $H_c = 0$, we have $\chi''(0) = 1$ which we will use in converting between the meter readings and $\chi''(H_c)$ in absolute units. Writing, for convenience,

$$F \equiv 1/n, \tag{5}$$

we rewrite Eq. (3) in the form

$$\chi''(H_c) = (1 - n^{-1})^2; \tag{6}$$

furthermore, from Eqs. (4) and (5) we have

$$b/c = (n-1) H_c^2. \tag{7}$$

If it is assumed that (2) is valid, Eq. (7) is convenient for experimental determination of the constant b/c. Actually, giving n an arbitrary value n_1 (greater than unity) and using Eq. (6) we can find $\chi''(H_{c_1})$ and then, going over to the corresponding point of the experimental curve by using the relation $\chi''(0) = 1$, we can find H_{c_1}; substituting n_1 and H_{c_1} in Eq. (7) we then find b/c. If, however, b/c is known from other sources, Eq. (7) can be used conveniently for experimental verification of the expression given in (2). Both procedures have been used in this work: Eq. (2) was verified in several materials in which the constant b/c was known and then the constant b/c was found by the method indicated above in a number of materials for which it had been hitherto unknown.

The absorption curve, the ordinates of which are proportional to the quantity $\chi''(H_C)$, was obtained using the method given by Zavoiskii.[5] In essence this method consists of using the experimentally determined linear relation between the grid current in an electronic oscillator and the magnitude of a small dissipative load. In measuring the absorption, a glass ampoule containing the material being investigated is introduced into a coil which is inductively coupled to the resonant circuit of the oscillator. The sample coil is oriented in a fixed magnetic field so that the oscillating field of the coil is parallel to the fixed field. When the fixed field is changed the dissipative load on the oscillator changes and there is a change in the grid current, which is detected by an appropriate instrument. A detailed description of the oscillator and its operation is given in Ref. 6. The sample is prepared from crystals which have been stored in the host solution to retain the water of crystallization. The neck of the ampoule containing the sample material (in powdered form) is sealed with paraffin. All measurements are carried out at 600 Mcs at room temperature.

3. The experimental spin-spin absorption curves obtained in the present work are all similar and differ only in intensity and half width. Hence it is sufficient to discuss one of them. In Table I are shown the results of an analysis of the curve for $MnSO_4 \cdot 4H_2O$; the quantity $\overline{\chi}''(H_C)$ denotes the readings corresponding to $\chi''(H_C)$. It is apparent from the table that Eq. (2) is in good agreement with the absorption curve; the value $b/c = 6.3 \times 10^6$ oersted^2 agrees with $b/c = 6.2 \times 10^6$ obtained by Tennyson and Gorter using a beat method (cf. Ref. 4). In all other cases investigated, which have been described in detail in Ref. 3, there is also substantial agreement between the experimental data and the theoretical expression (2) under the assumption that ρ is independent of H_C. It should be added that spin-spin relaxation has been investigated at ultrahigh frequencies by Kurushin[7] who has also obtained results which verify the Shaposhnikov theory[1] with ρ independent of H_C. On the other hand, there are recent experimental data on spin-spin absorption[8-11] which have as yet not received theoretical explanation.

TABLE I

n	$\chi''(H_c)$ $(\chi''(0)=1)$	$\overline{\chi}''(H_c)$ $(\overline{\chi}''(0)=84)$	H_c	$b/c \cdot 10^{-6}$ Oe^2
1.5	1/9	9.3	3400	5.9
2	1/4	21.0	2500	6.2
3	4/9	37.3	1780	6.4
4	9/16	47.2	1450	6.3
5	16/25	53.7	1240	6.0
6	25/36	58.3	1150	6.6
7	36/49	61.7	1040	6.5
8	49/64	64.3	960	6.4

Average: 6.3

TABLE II

Material	$b/c \cdot 10^{-6}$ Oe^2 Author's data	$b/c \cdot 10^{-6}$ Oe^2 Ref. 4 and others
$CrK(SO_4)_2 \cdot 12H_2O$	0.66	0.64
$[Cr\,4H_2O\,2Cl]\,2H_2OCl$	4.6	4.5
$Cr(NO_3)_3 \cdot 9H_2O$	1.2	1.1
$MnCl_2 \cdot 4H_2O$	19.3	19.5
$MnSO_4 \cdot 4H_2O$	6.3	6.2
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.65	0.65
$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	0.28	0.27
$[CuCl_4](NH_4)_2 \cdot 2H_2O$	2.5	—
$Cu(CH_3COO)_2 \cdot H_2O$	0.93	—
$CuSO_4 \cdot 5H_2O$	0.47	—
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	0.30	—
$CuCl_2 \cdot 2H_2O$	0.35	—
$Cr(OH)_3$	2.8	—

4. A summary of the results of the determination of b/c (both for materials in which it has been known and in which it is reported for the first time) is given in Table II. The values given in the last column of this table are taken from Gorter.[4]

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