Spin-Spin Absorption in Manganous Chloride Tetrahydrate

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Measurements on spin-spin absorption have been made on the antiferromagnetic substance, $MnCl_2 \cdot 4H_2O$, at temperatures from 1.3 to 4.2°K and at frequencies 1, 2, and 4 Mc/sec. The absorption shows a sharp peak at about 2.3°K and is proportional to the square of the frequency. At the highest temperatures an attempt has been made to compare the results with theory. The agreement is reasonable considering the extremely complicated situation where Stark splitting and dipolar, exchange and hyperfine coupling all are important. It is pointed out that an extension of this type of measurement to more simply behaved salts would be of considerable interest.

1. INTRODUCTION

IN a previous publication[1] it was pointed out that measurements on spin-spin absorption in antiferromagnetic substances at temperatures close to the Néel point would be of interest. We have carried out such measurements on $MnCl_2 \cdot 4H_2O$ in the temperature range 1.3° to 4.2°K. Other measurements which have been made already on the substance include: specific heat,[2] magnetic moment isotherms,[3] paramagnetic resonance,[4,5] and spin-lattice relaxation time.[6,7] The specific heat curve shows a characteristic anomaly at about 1.62°K which is almost certainly the result of an antiferromagnetic transition.

This particular salt was chosen for our first measurements for two reasons. It is possible to measure conveniently both above and below the transition temperature, T_c, and the specific heat of the salt is well known. The latter must be known in order to be able to compute the energy absorption from our measurements.

The method and apparatus used were the same as described previously,[1] with the exception that the measurements were taken in the liquid helium range of temperature rather than below 1°K. With the relatively simple calorimetric method employed, the thermal isolation of the specimen was not as complete as in previous experiments (mainly due to the difficulty of pumping out all exchange gas from the space around the specimen) and corrections for background heating had to be applied. Measurements were made on a powdered specimen at three rf frequencies: 1, 2, and 4 Mc/sec.

2. RESULTS

The relevant quantity first derived from the experimental data is the value of the complex component of the magnetic susceptibility, χ'' (emu/g ion). This is plotted in Fig. 1 as a function of the absolute temperature, T. No points were taken in the immediate vicinity of T_c. The reason for this was that the specific heat of the salt is so large near T_c that with the limited rf magnetic fields at our disposal only a very small rate of temperature rise could be obtained. The measurements in this region were not very accurate, therefore, but it was shown that there was no detectable irregularity in the absorption.

The most striking feature of Fig. 1 is that χ'' shows a sharp maximum at about 2.3°K, i.e., appreciably above T_c. The maximum occurs at a somewhat higher temperature the higher the frequency. Such maxima are observed also at low audio frequencies in many salts used in magnetic cooling.[8]

We have plotted χ''/ω as a function of T in Fig. 2, from which it can be seen that within the accuracy of measurement $\chi'' \propto \omega$ throughout the whole temperature
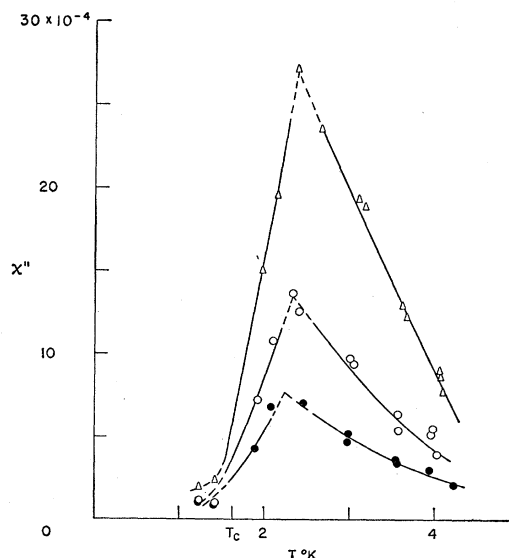
FIG. 1. Complex component of the magnetic susceptibility, χ''(emu/g ion) plotted as a function of the absolute temperature, T, for three measuring frequencies: ●, 1 Mc/sec; ○, 2 Mc/sec; and △, 4 Mc/sec.

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range. The dotted curve in Fig. 2 shows very roughly the behavior of the real part of the susceptibility, χ'. This was obtained from ac bridge measurements at 270 cps which contain two unknown constants. For χ', therefore, in Fig. 2 both the scale and zero on the ordinate are arbitrary. We have included the results, however, in order to contrast the temperature of the maxima in χ' and χ''.

3. DISCUSSION

A lengthy and critical discussion of the results does not seem to be appropriate at the present time, for not only is a certain amount of data lacking (e.g., the crystal structure is not known) but also the theory[9,10] can be strictly applied only when $T \gg T_c$. We feel that it would be of considerable interest to extend the theory, partly for its own sake and partly because it is intimately connected with the theory of lines hapes.[11–13]

In this salt three effects will have an influence[14] on the spin-spin relaxation time, τ_s, and hence upon χ'': the dipolar coupling, Stark splitting, exchange coupling, and perhaps also the hfs. Considering first only dipolar coupling, using the theory of Broer[9] and taking $H_i = 1500$ gauss (compare H_i for $MnSO_4 \cdot 4H_2O$),[15] we obtain $\nu_0 = 4200$ Mc/sec, and $\tau_s = [\nu_0(8\pi)^{\frac{1}{2}}]^{-1} = 4.7 \times 10^{-11}$ sec. This gives at $4°K$, for example, 5.1×10^{-11} for the value of χ''/ω. This may be compared to experiment in Fig. 2 where we have marked this point, D.

According to Broer the Stark splitting may be taken into account approximately by multiplying the above value of τ_s by a factor depending upon the splitting pattern for a simple ion. Assuming the sixfold degenerate level of the free ion to be split into three doublets, we find a value 0.505 for this factor. The effect of this is again shown in Fig. 2 (point S).

The effect of isotropic exchange upon τ_s, which has been discussed in some detail by Wright,[10] is similar to its effect upon the shapes of Larmor lines in that the ratio of the root mean fourth moment to the root mean second moment is increased, i.e., the absorption at low frequencies ($\nu \ll \nu_0$; our case) is increased at the expense of absorption at somewhat higher frequencies. Accordingly the value of τ_s obtained above has to be multiplied by a factor $(1+f)$, where f is a constant proportional to the square of the exchange energy between adjacent
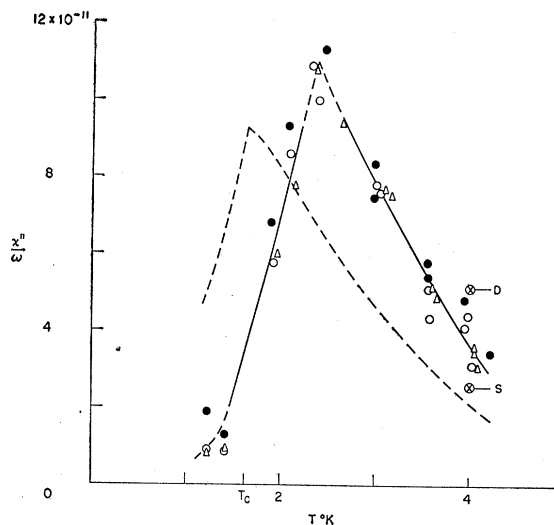
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FIG. 2. Complex component of the magnetic susceptibility divided by the angular frequency of measurement, χ''/ω, plotted as a function of the absolute temperature, T: ●, 1 Mc/sec; ○, 2 Mc/sec and △, 4 Mc/sec. Point D shows the calculated value considering only magnetic dipole forces, point S shows the value when crystalline electric field effects are included. The dotted curve shows roughly, and with an arbitrary ordinate scale, the course of the real part of the susceptibility.

spins. Unfortunately values of f are given explicitly only for a simple cubic lattice with $S = \frac{1}{2}$ so that it is not straightforward to obtain f, for example, from measurements of specific heat.[2,6,7] A reasonable value for f would probably move the point above our experimental curve. On the other hand, hyperfine splitting would tend to bring it down again.

In view of the very complicated situation which obtains in the case of Mn^{++}, there does not seem to be any point in pursuing the analysis further. In any case we could not hope to find an explanation along these lines for the maximum in χ'', which must be connected with the disappearance of the Larmor line observed in other antiferromagnetic substances near the transition point. Since short-range order is known to persist[2] above T_c, we may loosely interpret the fall in χ'' below the maximum to indicate that there occurs an appreciable reduction in amplitude of the Fourier components of the local field with frequencies higher than the measuring frequency. Some evidence is provided for this by the fact that the maxima for the higher frequencies occur at very slightly higher temperatures. In order to eliminate the effect of the crystalline electric field, we propose to confine our future measurements to single crystals with effective spin $\frac{1}{2}$. Crystals possessing a single axis of very high susceptibility should be especially interesting and should be more amenable to theoretical treatment.