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FINE STRUCTURE ON NMR LINES IN A PARAMAGNET DUE TO INDIRECT NUCLEAR SPIN-SPIN COUPLING

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Abstract.—We have observed fine structure in the spectra of the ligands in Rb2CuCl4.2H2O and isomorphous compounds in the paramagnetic state. Several experimental results prove that indirect nuclear spin-spin coupling is the origin of this structure. We argue that the range of the coupling is limited to two spins in these compounds.

Indirect coupling of nuclear spins in magnetic materials has been reported until now only as an important contribution to the NMR line width. Suhl /2/ and Nakamura /3/ have shown that the magnitude of this interaction, which occurs via the hyperfine coupling, is of the correct order to explain the observed line width.

The here presented experiments, however, are carried out in such a situation, that the indirect coupling involves only two nuclei. This coupling gives rise to a well resolved fine structure of the resonance lines, only when the two nuclei are identical. The nuclear spin hamiltonian is usually given by

$$H_N = \sum_i \frac{1}{2}(I_i^z + I_i^z)$$

When the magnetization is nearly saturated, the electron spin system is described by spin waves. Then, the coupling between the nuclear spin and the electron spin, which contains besides hyperfine also dipolar interaction, gives a correction to the nuclear spin hamiltonian

$$H_{NC} = \sum_{i,j} \frac{\text{exp}(i.k.r)}{4\pi^2} \left( A_{xx} + A_{yy} \right)^2 I_i^z I_j^z + \left( A_{xx} - A_{yy} \right)^2 I_i^z I_j^z$$

$$I_i^z I_j^z \pm \left( A_{xx} - A_{yy} \right)^2 I_i^z I_j^z + I_i^z I_j^z$$

Here, z is the direction of the magnetization and \( k \) is the wave vector. The indirect coupling is only effective when \( I_i \) and \( I_j \) are identical spins, and leads then to a fine structure.

Thus, the line shape of a particular isotope depends on the abundance of identical spins. The interaction between identical spins is appreciable only within a radius \( b_0 \). Here, \( s = \left( \omega_e / \omega_0 \right) / a \). Here, \( a \) is the lattice constant and \( \omega_e \) and \( \omega_0 \) are the electron angular frequencies related respectively to the exchange interaction and the applied field, including demagnetizing and anisotropy fields /3,4/. In most well studied magnetic materials is \( b_0 \) small and hence a large number of nuclei interact. This leads to a complicated fine structure that only a broadening of the nuclear resonance line is observed. In Rb2CuCl4,2H2O and isomorphous compounds however, the exchange interaction is rather small /1/. Now the radius \( b_0 \) can be made smaller than a at moderately strong external fields. In such a situation the interaction is restricted to the nuclei belonging to one copper octahedron. The octahedral surrounding of the copper ion contains two equivalent strongly bonded Cl ions denoted Cl (II), two weakly bonded Cl (I) ions and two H2O molecules, also strongly bonded. 

In figure 1 c the second derivative is shown of the central 35Cl NMR line in a 98% enriched 35Cl Rb2CuCl4,2H2O sample, at \( T = 1.2 \) K and \( H_0 = 10 \) kOe applied along the c axis. Whereas this line shows a clear fourfold splitting, the satellite lines (at 12.7 MHz and 2.5 MHz) exhibit a threefold
structure. In figure 1a the same resonance line is shown in an isotopically non enriched sample.

![Central NMR lines in Rb$_2$CuCl$_4$.2H$_2$O.](image)

Fig. 1: Central NMR lines in Rb$_2$CuCl$_4$.2H$_2$O. a and b in a sample with 75% $^{35}$Cl and 25% $^{37}$Cl; c in a sample with 98% $^{35}$Cl.

Now a quarter of the resonant $^{35}$Cl nuclei have a $^{37}$Cl neighbour, which explains the extra line in the middle of the resonance pattern. Reversely, when observing the $^{37}$Cl line, figure 1b, only a quarter of the $^{37}$Cl nuclei can interact with an identical nucleus and hence three quarters of the line intensity appears in the middle of the resonance pattern. Although less intensive, the four fine structure lines can also be seen in this figure. The tensor $\tilde{A}$ is rather anisotropic. Typical values for $^{35}$Cl are $A_{XX} = 27$ MHz, $A_{YY} = 4$ MHz and $A_{ZZ} = 3$ MHz, where $Z$ points along the Cu-Cl (II) bond and $Y$ along the c axis.

The angular dependence of the fine structure has been observed in the X-Y plane, whereas the spectrum along the Z axis shows no fine structure. This is in accordance with the expression for $\mathcal{H}$. Since the quadrupolar interaction in comparable to the Zeeman interaction ($\nu = 10.3$ MHz and $\eta = 0.16$) the effect of $\mathcal{H}$ on $\mathcal{H}$ cannot be calculated analytically. In the high field approximation the observed resonance patterns can be explained. Also the magnitude of the splitting is found to be correct. The ratio of the splittings in the $^{35}$Cl(II) and $^{37}$Cl(II) spectra is found to be $(^{35}A/^{37}A)^2$, again in accordance with $\mathcal{H}$. The same structure has also been found in the compounds $/1/$, in which RbCl is replaced by KCl, NH$_4$Cl, CsCl or NH$_4$Br, RbBr. As the abundance of $^{79}$Br and $^{81}$Br is equal, the resonance lines of both isotopes are similar. Again, the ratio of the splittings is found to be $(^{79}A/^{81}A)^2$. The temperature and field dependence of the fine structure has been studied extensively in Rb$_2$CuCl$_4$.2H$_2$O. The magnitude of the splittings is not temperature dependent for $T \leq T_C$ ($T_C = 1$ K). For $H_0 \geq 5$ kOe the splitting is proportional to $H_0^{-1}$, in accordance with the high field approach for $\sum_{\omega_k}^{-1}$. For $H_0 \leq 5$ kOe, the resonance lines are broadened by multiple spin-spin interactions, due to the increase of the interaction radius $b_0$. The same arguments hold for the line width in the ferromagnetic state in zero field.

In addition to the fore mentioned indirect coupling, $\mathcal{H}$ contains also a term for $i = j$, which gives a correction, of the same magnitude as the fine structure, to the parallel hyperfine interaction and to the quadrupolar interaction $/3,4/$. Recently, we reported on the $^{170}$ hyperfine interaction in these compounds $/5/$. We observed that the angular dependence of the quadrupolar splittings could not be described on the basis of the usual hamiltonian $\mathcal{H}$. Preliminary calculations show that by incorporation of these self energy terms of $\mathcal{H}$, the experimental data can be understood.

In low fields, at temperatures near $T_C$, a different kind of nuclear spin-spin interaction is observed $/1,5/$. As now $\chi_H$ is large, the expectation value $<S>$ will be influenced markedly by the Cu nuclear spin. This effect gives a correction to the larmor frequency of the ligand nuclei, proportional to $\chi_H A_{II}(\text{Cu})A_{II}(\text{Cl})$. A four fold equidistant pattern is observed in the spectra of $^{35}$Cl(II), $^{37}$Cl(II) and $^{170}$ when a weak magnetic field is applied along the Cu-Cl(I) direction, where $A_{II}(\text{Cu})$ is large $/1/$.

Further experimental and theoretical investigations are in progress.

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