

effect, as it is concerned essentially with a satellite zero-frequency line, and so has not been observed, as it is masked by the main decay phenomenon of Kronig and Bouwkamp.

C. J. GORTER: Indeed, in the pure dipole-dipole case with $S=1/2$ the difference between χ_{ad} and Broer's χ_{is} which is due to the satellite zero-frequency band is 20%. 80% goes to Broer's bands at the Larmor and the double Larmor frequencies.

A. H. COOKE: Do I understand that the line shape has been measured in the case where exchange narrowing occurs, and that it is not Gaussian?

C. J. GORTER: Yes, the $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ presents an example. A better example is DPPH where the exchange is relatively larger.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN

VOL. 17, SUPPLEMENT B-I, 1962

PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Splitting of the NMR Lines in Vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

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Nuclear magnetic resonance diagrams of the protons as well as phosphorus nuclei were determined in vivianite at temperatures between 1°K and 77°K. Vivianite becomes antiferromagnetic at a temperature between 4°K and 11°K. The phosphorus nuclei exhibit an isotropic shift. There are two types of Fe^{++} ions with a different magnetic behaviour.

Resonance diagrams with an external field rotating in the ac plane and in a plane perpendicular to the c -axis were obtained. The crystal of vivianite is monoclinic, the ac plane is a reflection plane. Thus, if the external field H_0 is rotated parallel to the ac plane the number of resonance lines found is half of that found for H_0 rotating in a plane perpendicular to the c -axis, in the paramagnetic state as well as in the antiferromagnetic state.

The diagrams show that the crystal is paramagnetic at liquid hydrogen temperatures and antiferromagnetic at liquid He temperatures. The resonance of the phosphorus nuclei exhibit apart from the anisotropic shift also an isotropic shift towards higher frequencies. The isotropic shift must be due to the interaction with an amount of magnetic spin moment transferred from the Fe^{++} ions to the phosphorus atoms. The temperature dependence of the splitting of the lines in the paramagnetic state is not the same for all nuclei. Two types of nuclei can be distinguished, the splittings of the first group

having a much larger dependence on temperature than the splitting of the other group (Fig. 1). At liquid He temperatures the crystal is antiferromagnetic. Sixteen lines were found for $H_0 \perp c$ axis (Fig. 2). The internal fields at the position of the nuclei were measured without the use of an external field. Also here two types of temperature

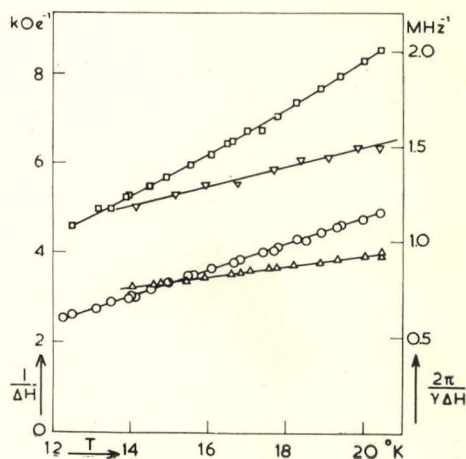


Fig. 1.

dependences can be distinguished. The resonance frequency of two of the proton lines

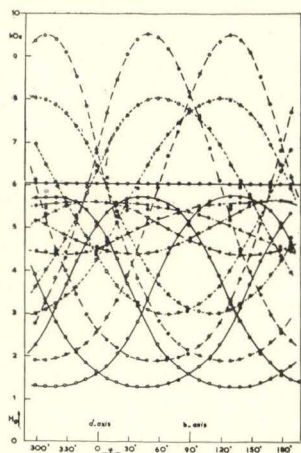


Fig. 2.

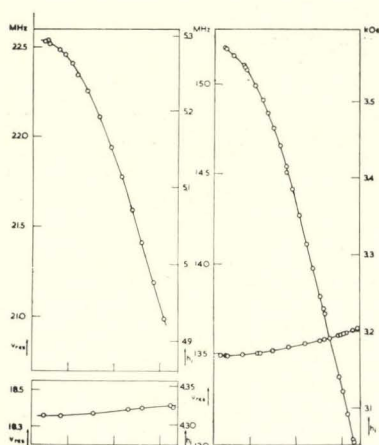


Fig. 3.

remains almost constant, while the resonance frequency of the two remaining proton lines and of the phosphorus nuclei decreases markedly when the temperature rises from 1.2°K to 4°K (Fig. 3).

These properties can be understood from the structure of the unit cell, which contains two types of Fe^{++} ions (Fig. 4). Each water molecule is close to a Fe^{++} ion of one type and much more distant from a Fe^{++} ion of the other type. So the field on a certain nucleus reflects mainly the magnetization of one of the types of Fe^{++} ions. The symmetry of resonance lines in the antiferromagnetic state shows 1) that the magnetic moment of each Fe^{++} ion is either exactly perpendicular to the b -axis, or parallel to the b -axis, 2) that the spin arrangement of the whole crystal is symmetric with respect to the ac plane. Susceptibility measurements show, that all Fe^{++} spins are most probably parallel to the ac plane.

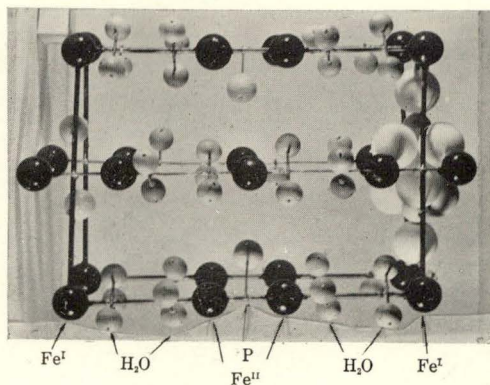


Fig. 4.

DISCUSSION

W. MARSHALL: Is it true that your experiments show that the close Fe ions, separated by 2.5Å, are ferromagnetically coupled? If so it seems likely that this is an example of ferromagnetic direct exchange.

N.J. POULIS: The experiments on phosphorus show that the magnetic moments of the pairs of Fe ions have to be parallel. This is thus a ferromagnetic arrangement of the two spins.

J. ITOH: May I ask the reason why you did not observe two proton splitting in all orientations of the crystal?

N.J. POULIS: No splitting of the proton line due to proton-proton interaction was found for vivianite in the paramagnetic or the antiferromagnetic state. The width of the resonance lines was small enough that we should have seen the proton-proton interaction if it was present. Until now we do not know the reason why it does not occur for these crystals. In the other crystals like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuK}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, proton-proton interaction was found,