Nuclear Ferromagnetism in a Perovskite Structure

P. Bonamour, V. Bouffard, C. Fermon, M. Goldman, J. F. Jacquinot, and G. Saux
Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, Orme des Merisiers, 91191 Gif-sur-Yvette CEDEX, France
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Ferromagnetism of ^{19}F nuclear spins in a monocrystalline $KMgF_3$ sample has been observed by NMR in the presence of a high magnetic field and in the microkelvin temperature range. The three ^{19}F spins of one crystalline cell are equivalent when the field is along the [111] axis of the crystal and inequivalent for the field along the [100] axis. At negative temperature, the structures are ferromagnetic with domains for both orientations. In the [100] orientation, it is a two-sublattice ferromagnetism: Spins belonging to different sublattices of ^{19}F have different polarizations within the same domain.

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Nuclear magnetic ordering (NMO) has been produced and investigated through different experimental methods in a variety of substances: insulators with light nuclear species,[1-6] Van Vleck compounds,[7-9] helium 3,[10,11] and metals.[12-15] The spin-spin interactions responsible for NMO are of a different nature: dipole-dipole interactions in insulators with light nuclei and in Van Vleck compounds, both dipole-dipole and RKKY interactions in metals and two-spins and four-spins exchange in ^3He. Dipolar interactions are unique in that they are known exactly, in both form and magnitude, without any adjustable parameter. They are the only spin-spin interactions in $KMgF_3$.

For insulators and some Van Vleck compounds, NMO can be produced in high fields, as a result of the very slow nuclear relaxation at low lattice temperature. This is done in a two-step process.[1,16-18] The first step is a dynamic polarization of the nuclear spins (DNP) through off-resonance microwave irradiation of paramagnetic centers at low concentration which decreases the nuclear entropy; the second step is a nuclear adiabatic demagnetization in the rotating frame (ADRF) performed by applying an rf field far off nuclear resonance and sweeping slowly the external field towards resonance. The nuclear ordering takes place under the effect of the secular part of the dipolar interaction, i.e., that part which commutes with the Zeeman Hamiltonian. Its form depends on the orientation of the external field with respect to the crystalline axes. Furthermore, the spin temperature can be chosen at will to be either positive or negative by performing the ADRF from below or above resonance.

The insulator $KMgF_3$ offers a wealth of new problems for NMO in high field because of its crystalline structure. $KMgF_3$ is a cubic perovskite[19] where fluorine nuclei are located on three out of four simple cubic sublattices of a fcc lattice. The fourth simple cubic sublattice is occupied by potassium nuclei and the magnesium nuclei are at the centers of the cubic cells. These last two kinds of nuclear spins have small gyromagnetic ratios and they play a negligible role in the ordering of the fluorine spins. As regards their secular dipolar interactions, the three sublattices of ^{19}F spins are in general not equivalent. Furthermore, they experience axially symmetric chemical shifts whose parallel axes are mutually orthogonal, with $\sigma_\perp - \sigma_\parallel \simeq 10$ ppm.[20] These features give rise to nuclear ordered structures different from those observed so far.

Experimentally, the single crystal of $KMgF_3$ was in the shape of a sphere of 2.15 mm diameter, submitted to a field of 4.8 T and cooled to 50–100 mK in a dilution refrigerator. The paramagnetic centers used for the DNP were F centers produced by bombarding the sample with 2.7-MeV electrons. For optimum results, the irradiation time was 80 min, with a current density of 10 $\mu A/cm^2$, on a sample cooled by circulation of helium gas at 230 K. The relative impurity concentration was about 10^{-4}. This is the most critical step of the experiment: having enough impurities to yield an efficient DNP, but not so many as to disturb too severely the ordering of the nuclear spins. The microwave source at 135 GHz was a carcinotron delivering about 1 W. Fluorine polarizations of 70% were currently obtained after 12 h of microwave irradiation. The ADRF was performed with a rf field of 3×10^{-6} T rotating component and a field sweep of 3×10^{-5} T/s. The ordering was studied by cw NMR measurements on ^{19}F and ^{39}K, at the respective frequencies of 192.8 and 9.56 MHz.

The NMO was investigated at negative spin temperature, with the external field parallel either to the [111] or to the [100] crystalline axis. It is for these two cases that the theoretical critical entropy is highest. For both cases, mean-field calculations predict ferromagnetism with domains in the form of thin slices perpendicular to the external field. For the orientation [111], all fluorine spins are equivalent. The Weiss field value for the critical temperature is $T_c = -0.51$ μK. The case of the orientation [100] is different: Two simple cubic sublattices of ^{19}F are equivalent and differ from the third one. This gives rise to a two-sublattice ferromagnet with domains where in each type of domain, spins of a

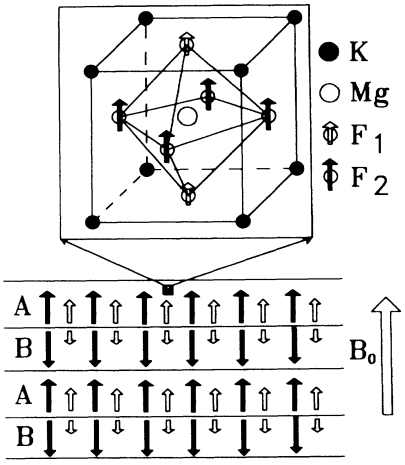

FIG. 1. Two-sublattice ferromagnet with domains for the external field B_0 parallel to [100] at negative temperature. The spins 1 and 2 are identified in the elementary cell.

different kind have different polarizations (Fig. 1). Furthermore, because of the chemical shift anisotropy, both kinds of spins have different Larmor frequencies. For an ADRF stopped at the average Larmor frequency, the effective Hamiltonian contains, in addition to the secular dipolar term, small Zeeman terms of opposite sign for each kind of spin. As a consequence, spins of a given kind have polarizations whose modulus differs in domains of opposite polarizations. This structure bears some similarity to those observed for instance in binary alloys or ferrimagnets, but the existence of different external fields on different sublattices would be difficult to produce in electronic systems.

Figure 2 shows the absorption signals of ^{39}K before and after ADRF for the field orientations [111] and [100]. The initial ^{19}F polarization was 70%. The production of ferromagnetism with domains shows up by the splitting of the signal: ^{39}K spins located in different domains experience different dipolar fields from the ordered ^{19}F species. More quantitatively, we will use the results of the Weiss-field approximation, to be detailed in the forthcoming article. We call 1 and 2 the different kinds of spins, of relative proportion $\frac{1}{3}$ and $\frac{2}{3}$, and label with A and B the domains of positive and negative polarizations, respectively. The expressions for the frequency splitting of the ^{39}K signal are of the following forms.

For the orientation [111]

$$\Delta\omega_K = 6qp^A, \tag{1}$$

where $p_1^A = p_2^A = -p_1^B = -p_2^B$.

For the orientation [100]

$$\Delta\omega_K = (q+q_1)(p_1^A - p_1^B) + 2(q+q_2)(p_2^A - p_2^B). \tag{2}$$

The coefficients q, q_1, and q_2 are calculated from the Fourier transform of the coefficients of the secular dipolar Hamiltonian. Their values are

$$q = +0.353 \text{ kHz}, \quad q_1 = +0.717 \text{ kHz}, \quad q_2 = +0.171 \text{ kHz}. \tag{3}$$

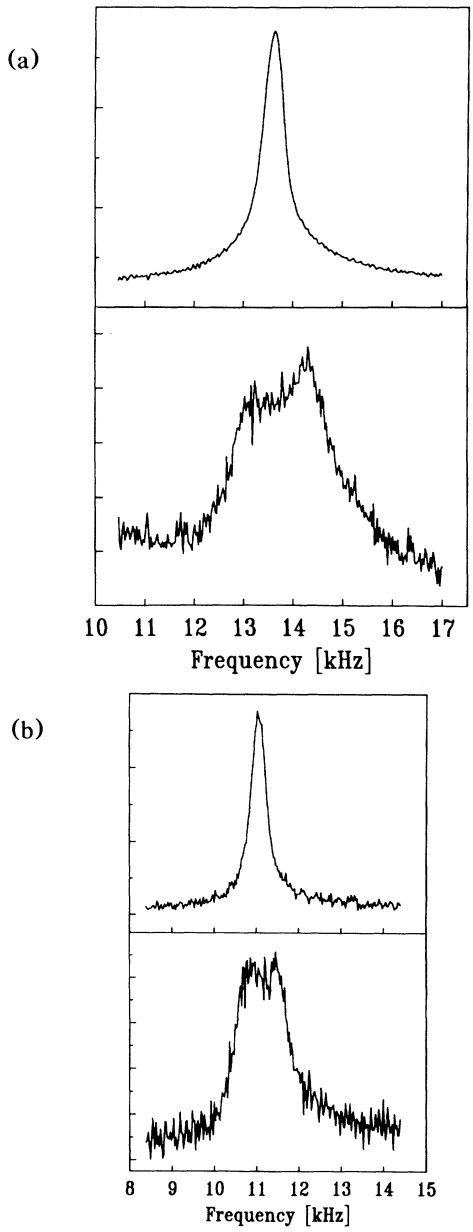

FIG. 2. ^{39}K absorption signals. The upper signal is taken before the ADRF and the lower signal after the ADRF. (a) Orientation [111], negative temperature; (b) orientation [100], negative temperature. The origin of frequencies is arbitrary.

In Fig. 2, the splitting is $\Delta\omega_K = 1.15$ kHz for the orientation [111] whence $p^A = -p^B = 0.54$ and, according to the Weiss-field approximation, $T = -0.46\ \mu$K.

For the orientation [100], the splitting is $\Delta\omega_K = 0.55$

kHz yielding, in the same approximation,

$$p_1^A = +0.086, \quad p_2^A = +0.419,$$

$$p_1^B = -0.292, \quad p_2^B = -0.411,$$

and $T = -0.522\ \mu$K.

The large difference between the absolute values of p_1^A and p_1^B is a consequence of the difference of Larmor frequencies between spins 1 and 2.

Figure 3 is a plot of the transverse susceptibility $\chi_\perp$ as a function of dipolar energy. Both quantities are derived from the ^{19}F absorption signal. Its first moment yields the dipolar energy and its Hilbert transform yields the transverse susceptibility.[17] At low energy, the high-temperature approximation for spin-temperature theory yields a linear relation between $\chi_\perp$ and the dipolar energy, as observed. However, the experimental slope is much lower than expected, which reflects the important contribution of the paramagnetic impurities to the energy. These impurities are also responsible for the smoothing of the variation of $\chi_\perp$ at the passage from paramagnetism to ferromagnetism. Nevertheless, especially for the orientation [100], the value of $\chi_\perp$ in the ferromagnetic phase is in reasonable agreement with theory.

For a two-sublattice ferromagnet with domains, in the orientation [100], one expects four resonances for ^{19}F, two in absorption and two in emission, produced by the spins parallel and antiparallel to the external field. They are observed below and above the average Larmor frequency, respectively. The existence of absorption and emission parts in the NMR signal is standard for systems with infinite Zeeman temperature and finite dipolar temperature.[17] NMR signals of ^{19}F are shown in Fig. 4. They were recorded at different times after the ADRF and, because of the spin-lattice relaxation, they correspond to increasing values of $|T|$. The structure is ferromagnetic for the first two signals and paramagnetic in the last one. The four resonances observed in the ferromagnetic phase show clearly the existence of four different dipolar fields experienced by two kinds of spins in the two types of domains. The signals are not centrosymmetric, a consequence of the chemical shift anisotropy. Their overall shape is as expected from theory despite some broadening due to the dipolar field of the paramagnetic impurities and to a possible small inhomogeneity of the initial nuclear polarization. By contrast, for the orientation [111] the ^{19}F resonance signal after the ADRF is always centrosymmetric with only one peak in absorption and one peak in emission.

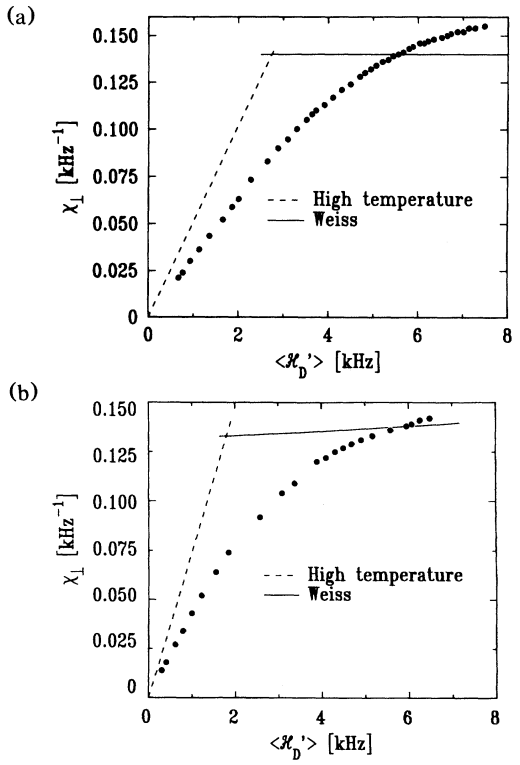

FIG. 3. Transverse susceptibility $\chi_\perp$ as a function of the dipolar energy $\langle \mathcal{H}_D' \rangle$. (a) Orientation [111], negative temperature; (b) orientation [100], negative temperature.

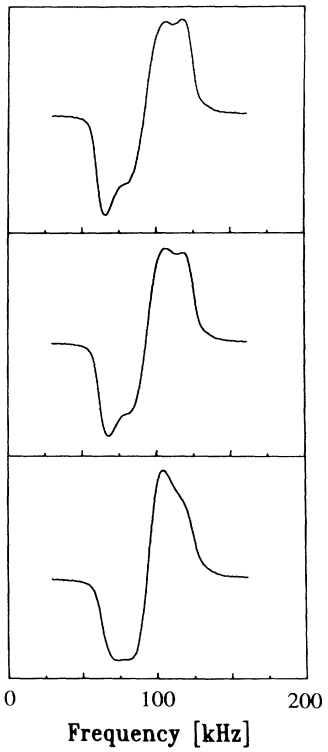

FIG. 4. ^{19}F absorption signals of orientation [100] at negative temperature. Upper and middle signals: ferromagnetic phase with domains; lower signal: paramagnetic phase. The origin of frequencies is arbitrary.

These results establish unambiguously the existence of the ferromagnetic phases predicted on theoretical grounds for a system noticeably different from those whose nuclear magnetic ordering has been studied up to now.

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