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μSR-INVESTIGATION OF A LIQUID CRYSTAL
CONTAINING IRON ATOMS

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Liquid crystal physics is one of extensively developing fields in condensed matter physics and is of practical and fundamental importance. The liquid-crystal state is found not only in compounds produced in the laboratory. It is widely spread in the living nature and might be indispensable for functioning of all living systems.

Recently, liquid crystals (LQ) with atoms of transition metals have attracted considerable interest. "Pure" organic LQ are diamagnetic. Metal-containing liquid crystals (metallomesogens) may have certain magnetic properties depending on their metal atom and its chemical bond. This is quite attractive in terms of a possibility of producing LQ with new properties.

The chemical formula of the investigated liquid crystal is shown in fig.1. A peculiarity of the macrostructure of this LQ-compound is that it forms a layered smectic-A liquid crystal phase at the temperatures $120 - 150$ ^{0}C. It is presumed that in such a structure the iron atoms reside in the plane of the smectic layer, the distance between the iron atoms in the layer plane being a few times smaller than the distance between the iron atoms of different layers. Thus, a two-dimensional magnetic ordering is possible due to the interaction of magnetic moments of the iron atoms of the same layer.

From the measurements of paramagnetic susceptibility it is known [1] that in the considered type of the compound $FeClL_2$ (L-bidentate azomethine ligand) the iron ions have the magnetic moment equal to 5.9 μ_B, which corresponds to the high-spin state (d^5, S=5/2) of the iron ion Fe^{3+} in the liquid crystal. In the Mossbauer absorption spectra of $FeClL_2$ [2] a hyperfine structure (HFS) arising from the hyperfine interaction of the magnetic moments of the nucleus and the electron shell of the iron atoms is resolved at temperatures below 80 K. As the temperature decreases, the fraction of HFS increases up to 36 % at 4 K. In the longitudinal magnetic field of 6 T the HFS fraction in the Mossbauer absorption spectra of the LQ under investigation is 94% at 4 K. This means that the relaxation rate of the magnetic moment of the electron shell of an iron ion is less than 10^6 s^{-1}. It also follows from the Mossbauer spectroscopy at room temperature that the iron ions Fe^{3+} are in two chemically non-equivalent positions in proportion $\sim$ 50 : 50. On the basis of the magnetic susceptibility and Mossbauer data it is assumed that there is an exchange interaction between the iron atoms at the temperatures below 80 K, which leads to two-dimensional (or one-dimensional) anti-ferromagnetic ordering of their magnetic moments.

The goal of the present work is to prove (or disprove) magnetic ordering in metallomesogens by an independent method different from the one used
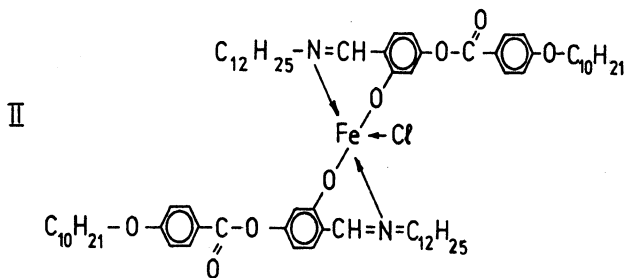
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Figure 1: Molecular structure of the investigated liquid crystal

in [1, 2]. The application of the neutron diffraction method, which is widely used to study magnetically ordered structures in crystals, is restricted by the presence of a large amount of hydrogen atoms in the liquid crystal molecule. Preliminary measurements with the DN2 spectrometer at FLNP (Frank Laboratory of Neutron Physics) of the Joint Institute for Nuclear Research showed that the large contribution from the scattering on hydrogen really does not allow one to study a possible magnetic structure formed by the iron atoms in the liquid crystal.

As is known, polarized positive muons are a good probe to investigate microscopic and macroscopic magnetic properties of matter (see, for example, [3]). In the present work the results of preliminary investigations of the temperature dependence of polarization of positive muons in the liquid crystal are presented. The measurements were performed at the Paul Sherrer Institut (PSI, Villigen, Switzerland) in a muon beam of ~ 40 MeV/c momentum in a magnetic field of 100 Oe transverse to the direction of the muon spin in the temperature range of $4.2 - 300$ K. The polycrystalline LQ weighting about 1 gram was packed in a thin polyethylene. The polyethylene package had 15x15 mm^2 dimensions and weighted about 15 milligrams. The thickness of the sample along the direction of the muon beam was ~ 0.4 g/cm^2. The sample was mounted on a plate (30x30x1 mm^3) made of melted quartz. To cool the sample a helium-flow cryostat was used. Quartz is used as a sample mount because a muon forms a muonium in quartz with the 85% probability and the quartz contribution to the spectrum practically does not preclude investigations of the behavior of the paramagnetic (free or chemically bound) muon in the sample.

To determine the polarization of the muon beam and the contribution of the quartz mount, measurements were performed with the mount and with a high-purity aluminum sample (in aluminum muonium is not formed).

The experimental μSR-spectra measured in the external magnetic field transverse to the direction of the muon spin (TF-measurements) and in the absence of the external magnetic field (ZF-measurements) were approximated by the respective functions:

$$N(t) = N_0\, e^{-\tau_\mu t}\, [\, 1 + a_\mu e^{-\lambda_\mu t} \cos(\omega_\mu t + \phi_\mu)$$
$$+ a_{Mu}\, e^{-\lambda_{Mu} t} \cos(\omega_{Mu} t + \phi_{Mu}) \cos(\Omega_{Mu} t)\,] + B, \quad (1)$$

$$N(t) = N_0\, e^{-t/\tau_\mu} [1 + a_\mu e^{-\lambda_\mu t} + a_{Mu}\, e^{-\lambda_{Mu} t}] + B, \quad (2)$$

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where N_0 is the count rate in the zero histogram channel; $a_\mu(a_{Mu})$, $\lambda_\mu(\lambda_{Mu})$, $\omega_\mu(\omega_{Mu})$, $\phi_\mu(\phi_{Mu})$ are the precession amplitude at t=0, the relaxation rate, the frequency and initial phase of the precession for the muon (muonium) component of the polarization; Ω_{Mu} is the beat frequency for the muonium component; B is the background of accidental coincidences.

From the measurements in Al the amplitude and the frequency of the free muon spin precession in the external magnetic field were determined: $a_\mu(\text{Al}) = 0.217 \pm 0.001$, $\omega_\mu(\text{Al}) = (8.690 \pm 0.002)$ rad/μs.

Figure 2 presents the experimental data on the time dependence of the muon polarization in quartz. In fig. 2 a the data are shown after summation over 32 histogram channels; accordingly, the bin width is $\Delta t = 20$ ns. The precession amplitude at the free muon spin frequency is $a_\mu(\text{SiO}_2) = 0.032 \pm 0.001$. In reality the quartz spectrum has a two-frequency "fine" structure. It is clearly seen from the fragment of the spectrum (fig. 2 b) where Δt is 1.25 ns. From the fit of the experimental data by function (1) it follows that the amplitude of the muonium component in quartz is $a_{Mu}(\text{SiO}_2) = 0.084 \pm 0.003$ and the sum is $a_\mu(\text{SiO}_2) + 2\,a_{Mu}(\text{SiO}_2) = 0.200 \pm 0.006$. This value does not contradict the value of $a_\mu(\text{Al})$ within three standard errors (a possible "missing" fraction of the polarization is (7.8 ± 2.8) %).

The precession frequency of the muonium component and the beat frequency were also found from the measurements in quartz: $\omega_{Mu}(\text{SiO}_2) = (142.252 \pm 0.005)$ MHz and $\Omega_{Mu}(\text{SiO}_2) = (4.642 \pm 0.005)$ MHz.

Figure 3 shows time distributions of positrons from the decay of μ^+ in the liquid crystal in the transverse magnetic field and in the absence of the external magnetic field at $T = 150$ K ($\Delta t = 20$ нс).

Significant damping of the muon polarization at t=0 followed by a slow relaxation is seen for the spectrum measured in the absence of the external magnetic field. The analysis of the experimental data obtained in the transverse magnetic field shows that fast relaxation is due to the muonium component of polarization, while there is only slow relaxation on the muon component. Figure 4 shows the temperature dependencies of the muon $a_\mu(\text{LQ})$ and muonium $a_{Mu}(\text{LQ})$ components of polarization. As is seen from the figure, $a_\mu(\text{LQ})$ and $a_{Mu}(\text{LQ})$ are practically independent of temperature within experimental errors and their amplitudes are $a_\mu(\text{LQ}) = 0.093 \pm 0.001$ and $a_{Mu}(\text{LQ}) = 0.041 \pm 0.01$. Since the dimensions of the sample in the plane perpendicular to the beam axis are smaller than the beam spot size, the muonium component is most probably due to muons stopped in the quartz mount. Based on the above supposition and on comparison of $a_{Mu}(\text{LQ})$, $a_{Mu}(\text{SiO}_2)$ and $a_\mu(\text{SiO}_2)$, one can easily estimate
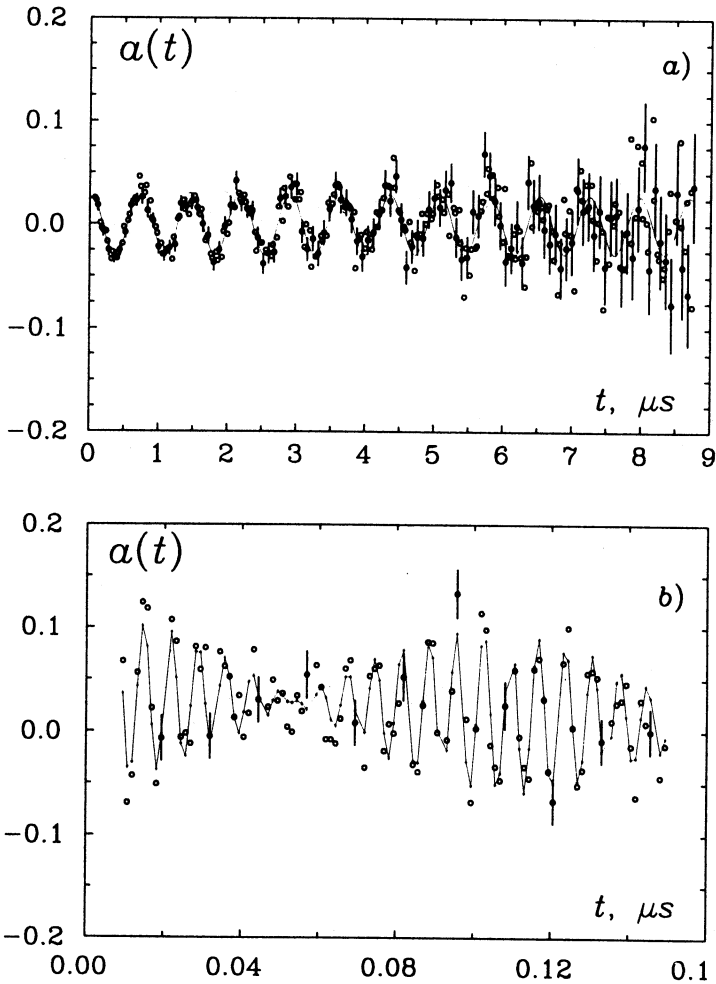
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Figure 2: Time dependence of the muon polarization in melted quartz: a) the histogram bin width Δt is 20 ns; b) $\Delta t = 1.25$ ns. The lines correspond to the least-squares fit
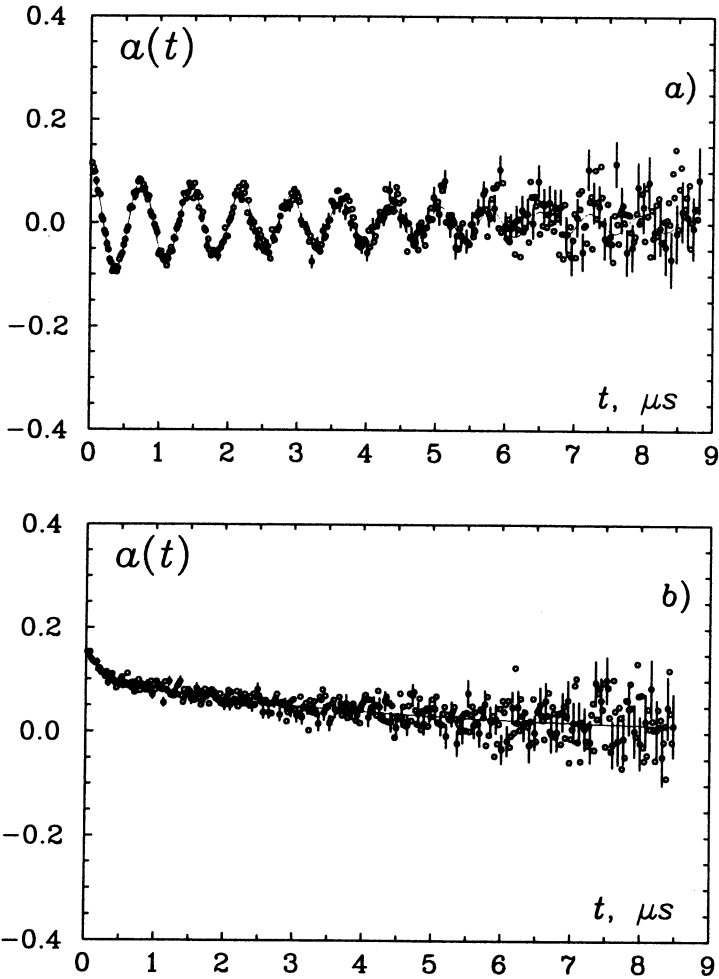
Figure 3: Time dependence of the muon polarization in the liquid crystal at $T = 150$ K: a) in the magnetic field 100 Oe transverse to the direction of the muon spin; b) in the absence of the external magnetic field
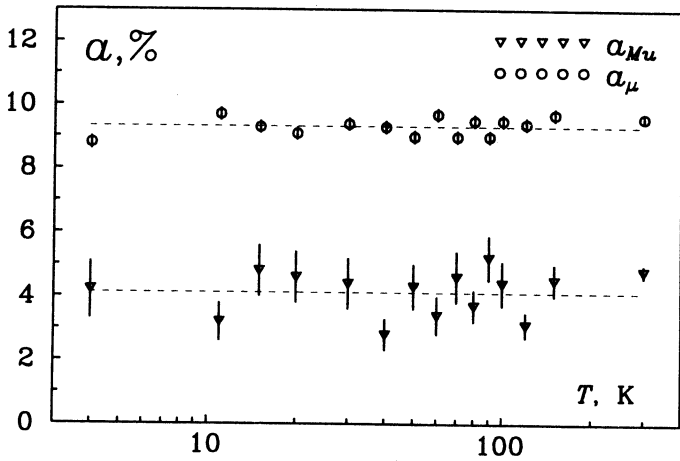
Figure 4: Temperature dependencies of the amplitudes of the muon (a_μ) and muonium (a_{Mu}) components of polarization in the liquid crystal. The dashed lines serve to guide an eye

the maximum contribution of quartz to $a_\mu(LQ)$ to be smaller than $(17 \pm 5)\%$ $((a_{Mu}(LQ)/a_{Mu}(SiO_2)) \cdot (a_\mu(SiO_2)/a_\mu(LQ)) \cdot 100\%)$. Figure 5 shows the temperature dependence of the relaxation rate of the muon component in the liquid crystal (a possible contribution of quartz is not taken into account). The relaxation rate increases from 0.1 to 0.3 μs^{-1} as the temperature decreases from 300 K to approximately 80 K and is practically constant in the temperature range $4.2 - 80$ K.

Before discussing the results, let us consider what one may expect within the frames of a simplified model for the possible interactions of the positive muon spin in the liquid crystal medium. Let us assume that the positive muon and iron ions are distributed randomly throughout the crystal and the magnetic moments of the iron ions have arbitrary orientation in space and do not change with time (static case). The magnetic moments of the iron ions produce dipole fields on the muon. The distribution of this local magnetic field on the muon H^{int} is Lorenz [4]. In the transverse external magnetic field the muon polarization depends on time as (see [5]):

$$G(x) = exp(-\lambda t), \tag{3}$$

where $\lambda = \gamma_\mu \sigma$; $\gamma_\mu = 1.355 \cdot 10^4$ Hz/G is the gyromagnetic ratio for the muon; σ is the dispersion of the internal magnetic field on the muon.

In the absence of the external magnetic field the time dependence of the muon polarization is described by the Kubo-Toyabe function [5]:

$$G(z) = \frac{1}{3} + \frac{2}{3}(1 - \lambda t)\exp(-\lambda t). \tag{4}$$

Let us estimate the magnetic field and its dispersion on the muon within the static approach. The mean value of the internal magnetic field H^{int} can be obtained by comparing the muon-spin precession frequencies in aluminum and in the liquid crystal. In aluminum a relaxation and a frequency shift of the muon-spin precession are absent at room temperature [6, 7]. The temperature dependence of the muon-spin precession frequency in the liquid crystal $\omega_\mu(LQ)$ is shown in fig. 6. The dashed line in the figure is the value of $\omega_\mu(Al)$. The mean value of $\omega_\mu(LQ)$ differs from $\omega_\mu(Al)$ by $\Delta\omega = (17 \pm 4) \cdot 10^{-3}$ rad/μs in the temperature range below 100 K. Accordingly, the mean value of the internal magnetic field produced by magnetic moments of iron ions on the muon is:
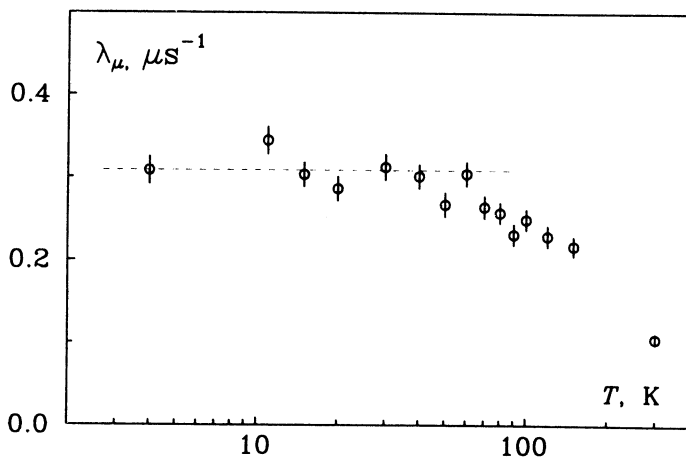
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Figure 5: Temperature dependence of the relaxation rate of the muon polarization component in the liquid crystal. The dashed line serves to guide an eye
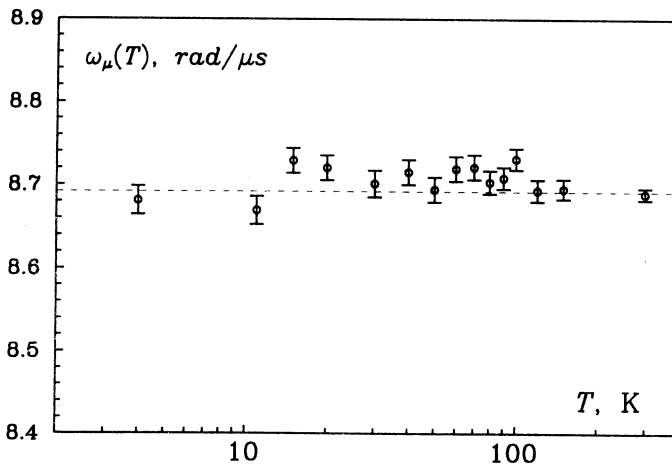
Figure 6: Temperature dependence of the muon-spin precession frequency in the liquid crystal. The dashed line corresponds to the muon-spin precession frequency in aluminum

$$H^{\text{int}} = \frac{\Delta\omega}{\omega_\mu(\text{Al})} \cdot H^{\text{ext}} = 0.2 \pm 0.05 \text{ Oe.}$$

The dispersion of the magnetic field $\Delta H^{\text{int}} = \lambda/\gamma_\mu$ is about 7 Oe at $T = 300$ K and 21 Oe at T $\leq$ 80 K. (In the static case the dipole magnetic field produced by an iron ion with the magnetic moment 5.9 μ_B at a distance of 10 Å is about 60 Oersted.)

The experimentally observed time dependence of the muon polarization in the liquid crystal in the zero external magnetic field does not agree with the Kubo-Toyabe one expected in the static case. It is worth mentioning that the mean value of the local magnetic field on the muon determined from the muon-spin precession frequency does not depend on the model for the interaction of the muon with matter. The value obtained for the dispersion of the local magnetic field can be considered as its maximum value because the muon-spin relaxation can also be caused by dynamic processes.

The experimental result may be explained in the following way. In organic compounds with double chemical bonds the muon (and/or muonium) promptly forms a chemically bound state (see, for example, [8, 9]). It is evident from the structure of the molecule that there are a number of preferable and practically equivalent sites for the positive muon to bind. Therefore, in the first approximation the muon may be thought of as randomly distributed throughout the crystal in a chemically bound state. In this case the muon-spin relaxation is determined by fluctuations of the magnetic fields produced by iron ions at muon locations. At room temperature the liquid crystal is paramagnetic and in accordance with the Mossbauer data the relaxation rate of an iron ion magnetic moment is higher than 10^{10} c^{-1} down to 80 K. Accordingly, the dispersion of the magnetic fields of the iron ions on the muon site is close to zero and the muon-spin relaxation rate is expected to be small. Indeed, the relaxation rate of the muon spin is not high at room temperature: $\lambda_\mu = (0.11 \pm 0.01)$ μs^{-1}. If LQ were paramagnetic in the temperature range under study, λ_μ would continuously increase with decreasing temperature. But the continuous increase in λ_μ with decreasing temperature is observed only in the range of $80 - 300$ K (see fig. 5). In the temperature range $4 - 80$ K λ_μ is constant within experimental errors. Variation in the temperature dependence of λ_μ at $T \approx 80$ K and constant λ_μ at $T < 80$ K can be considered as evidence for "freezing" and ordering of the magnetic moments of iron ions. Magnetic ordering at $T < 80$ K may be due to the exchange interaction (or indirect exchange interaction via chlorine or oxygen atom electrons) between the d-electrons of the iron ions of the same plane

(two-dimensional magnetic ordering). Ferromagnetic ordering is excluded because the observed mean value of the internal magnetic field on the muon site is close to zero both for $T > 80$ K and for $T < 80$ K.

Anti-ferromagnetic ordering may be due to the presence of two chemically non-equivalent iron ions in the liquid crystal. It is possible that chemically non-equivalent iron ions form their own sublattices with equal and oppositely directed magnetizations. In this case the internal magnetic fields in the liquid crystal will not change at $T < 80$ K and the relaxation rate of the muon spin will be constant, which is confirmed by the present measurements.

Thus, the results of the present work do not contradict the conclusion [2] that the iron ions form an antiferromagnetically-ordered structure in the investigated liquid crystal.

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Работа посвящена исследованию свойств жидкого кристалла, в состав молекулы которого входит атом железа. Соединения данного типа представляют интерес с точки зрения получения жидких кристаллов, обладающих магнитными свойствами. Были проведены измерения температурной зависимости поляризации и скорости релаксации спина положительных мюонов в жидком кристалле в диапазоне температур 4–300 К. Полученные результаты не противоречат предположению, что при температурах ниже 80 К ионы железа, входящие в состав молекулы жидкого кристалла, образуют антиферромагнитно-упорядоченную структуру.

Работа выполнена в Лаборатории ядерных проблем им. В.П.Джелепова ОИЯИ.

The work is devoted to the investigation of properties of a liquid crystal whose molecule contains iron atom. The compounds of this type are of interest from the point of view of obtaining liquid crystals with magnetic properties. The temperature dependence of the polarization and relaxation rate of positive muon spin in the liquid crystal was measured in the temperature range 4–300 K. The results obtained do not contradict the suggestion that the iron ions from an antiferromagnetically-ordered structure in this liquid crystal at the temperatures below 80 K.

The investigation has been performed at the Dzelepov Laboratory of Nuclear Problems, JINR.