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MUON SPIN RELAXATION STUDY OF PROTONIC SUPERIONIC CONDUCTOR $CsHSO_4$

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Introduction

Despite the extensive studies on the structure and properties of cesium hydrogensulphate $CsHSO_4$(CHS) which belongs to a new class of protonic superionic conductors (see[1-3] and references there in), the mechanism of high protonic conductivity in such materials is not yet finally ascertained. The phase diagram for the virgin CHS crystal is[2]:

$$\begin{array}{ccccc} \text{phase III} & \xrightarrow{330 \div 370K} & \text{phase II} & \xrightarrow{414K} & \text{phase I} \; . \\ P2_1/c & & P2_1/c & & I4_1/amd \end{array}$$

The temperature and kinetics of III→II transition depend on the amount of water in the powder sample. Keeping the CHS powder after the phase transition into phase II in vacuum or in dry atmosphere at a room temperature for a long period of time (about one month) or cooling the sample down to liquid nitrogen temperature does not result in a transition to the initial phase III[2]. Phase III does not exist in a deuterated sample ($CsDSO_4$) with a degree of deuterization more than 60%. In phases II and I protonated and deuterated samples are isomorphous. The transition temperature II→I for the deuterated sample is 412K[1].

One of the characteristic features of phases III and II is the existence of two possible positions for each proton. Due to energy nonequivalency of these positions a proton occupies only one of them. As a result,along one of the crystallographic directions hydrogen bounded chains are formed. To illustrate this fact the phase II structure projection on bc crystal plane is shown in fig.1 according to[4]. The superionic phase I is tetragonal. In this phase the number of possible proton positions are increased. All positions are crystallographically equivalent, so the proton can occupy each of them with equal probability and can diffuse over these positions[5,6].

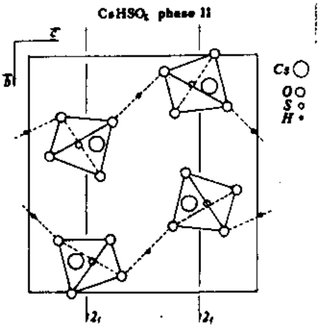

Fig. 1. The projection of the structure of phase II of $CsHSO_4$ ($CsDSO_4$) on bc plane according to [4].

This information formed the basis of the μSR experiment. One can suppose that due to proximity of muon and proton properties in matter and also because of structure peculiarities of crystals under investigation, implanted muons will occupy vacant hydrogen positions. The groups of symmetry of phases III and II are a subgroup of phase I. So an alternative possibility for muon location in phases III and II is the images of proton positions in phase I. The damping rate of muon spin precessing in an external magnetic field will be defined by random fluctuations of local magnetic fields of nuclear magnetic dipols of Cs and H (D).

By analogy with hydrogen diffusion one can expect a spasmodic increase of a diffusion coefficient for muons as a superionic transition temperature has been achieved. As a consequence, the damping rate of muon spin relaxation will decrease.

Experiment

The experiments have been performed with the pulsed muon beam at the ISIS pulsed neutron source, Rutherford Appleton Laboratory (UK). Such experiments are practically impossible on continuous sources because of low damping rates (about 0.1 - 0.2 μs^{-1}) even in phases III and II characteristic for random fields defined by dipolar interactions. To registrate such low rates and their decreasing one should have a set of good statistics. For reasonable experimental time it is possible only at a pulsed high intensity source.

Powder samples were being placed in a copper holder coated with a hematit mask to reduce a background. The sample size was about 3mm thick and 35 mm in diameter. A holder with a sample was mounted in a closed cicle refrigerator. Measurements were performed over the range of temperatures 15-440K. The external magnetic field 221G transverse to a muon spin was formed by the Helmholtz coils.

The muon beam size was 11mm (vertical) x 20mm (horizontal). The decay positrons were registered by 32 scintillators mounted in two circle holders around the sample. Detectors were grouped in 8 x 4 segments.

For each temperature the precession histogram was registered for 8-9 millions of events over all detectors. The CHS sample was subsequently heated from room temperature up to 440K then cooled down to 15K and was heated again to room temperature. As it has been mentioned above during this cycle the sample undergoes phase transitions III→II, then II→I on heating. On being cooled the sample returns into phase II but phase III does not restore because the sample is in vacuum during the experiment. For the CDS sample the measurements were performed on heating it from 15K to room temperature.

The experimental histogram for one of the detector's segments for CHS at 15K is shown in fig.2.

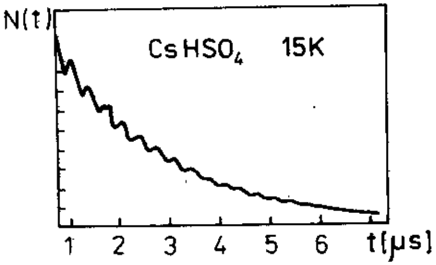

Fig.2. The experimental histogram from one of the detector's segments for CsHSO$_4$ at 15K.

Data have been processed using the formula:

$$N(t) = N_0 \exp(-t/\tau_\mu) \left[1 + a P(t) \right], \tag{1}$$

where τ_μ = 2.20 μs is the muon life time, a is the experimentally achieved asymmetry. The P(t) function corresponding to the histogram in fig.2 compensated for the radioactive decay curve is shown in fig.3. For P(t) one can use the formula:

$$P(t) = p(t) \cos(\omega_B t + \phi), \tag{2}$$

where p(t) is the damping of spin polarization, ω_B is the Larmor frequency muon precession in the external magnetic field. For p(t) the Gaussian lineshape has been used over the whole temperature range:

$$p(t) = \exp(-\sigma^2 t^2). \tag{3}$$

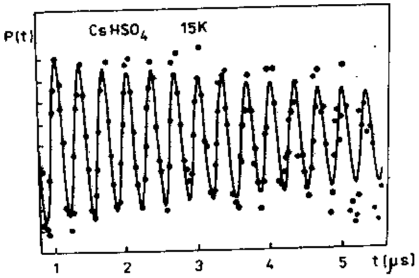

Fig.3. A μSR precession signal together with the on-line fit (solid curve). These data correspond to those in fig.2 compensated for the radioactive decay curve.

Experimental results

a) Damping rate

In fig. 4 the temperature dependence of a damping rate σ is shown. Experimental values and errors are averaged over all histograms. Up to T=100K the damping rate is constant: $\sigma = 0.12\ \mu s^{-1}$. One can calculate the quantity $\langle \delta H^2 \rangle$ characterizing the intensity of the magnetic fluctuations/8/:

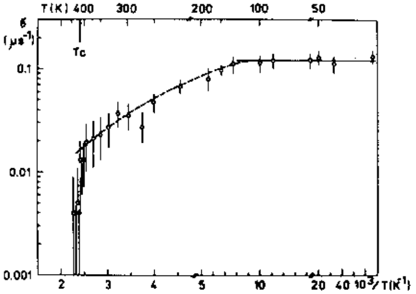

Fig.4. Temperature dependence of damping rate of muon polarization versus inverse temperature for $CsHSO_4$. Solid line is the best fit to a temperature range 15-100K. The broken line is only a guide to the eye. An arrow shows a supersonic transition temperature.

$$\sigma^2 = \frac{1}{2}\gamma_\mu^2 \langle \delta H^2 \rangle , \qquad (4)$$

where γ_μ =13.55 kHz G^{-1} is the muon magnetogyric ratio. The value $\sqrt{\langle \delta H^2 \rangle}$ = (13 + 1)G is in good agreement with the values characteristic for dipolar interactions.

At temperatures higher than 100K the damping rate decreases monotonically up to the superionic transition temperature due to activation diffusion of muons in a crystal. For quantitative analysis of this curve one should use the exponential law for p(t) rather than the Gaussian law (see eq.3)/8/. Hereafter we will reanalyze data taking this circumstance into account together with model calculations to define the exact positions of muon location in a crystal, an activation energy and muon correlation times. Preliminary estimation has given us E_a = (50 ± 1) meV.

There are no remarkable differences in the μSR linewidth for phases III and II of CHS.

For the CDS sample over the temperature range under investigation (the sample is in phase II at this temperature range) the linewidth is the same as for CHS in the limits of experimental errors.

When a superionic transition temperature (T_c =414K) is achieved a spasmodic decrease of a linewidth is observed for CHS. This fact points to a drastic increase of the muon diffusion coefficient. At a superionic phase the damping rate is too low to analyze its temperature dependence.

b) Asymmetry

The temperature dependence of asymmetry (see eq.1) for CHS and CDS is shown in fig.5. The asymmetry is small for both samples over the whole temperature range. The reason to this is not yet clear. It is conceivable that muonium is formed and asymmetry characterizes a muonium fraction in the sample.

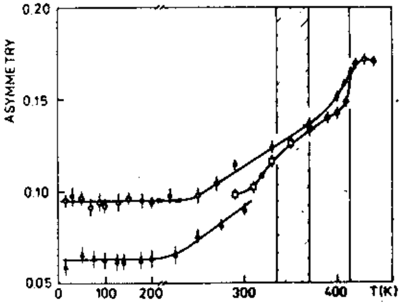

Fig.5. Temperature dependence of asymmetry. The shaded area is the region of phase III→phase II transition according to/2/. Vertical line is the temperature of phase transition into superionic phase I. Squares correspond to CHS in phase III, points are phases II and I of CHS. Triangles correspond to phase II of CDS. Open symbols - heating of samples, black symbols - cooling down.

In CHS the asymmetry increases with the temperature and at the superionic transition temperature its spasmodic change is observed. As noted above on cooling from the superionic phase the reverse transition into phase III did not occur and CHS could remain in phase II for a long period of time. As one can see in fig.5 the asymmetry for phases III and II is different at the same temperature. Temperature cycling of **the** CHS sample in phase II gives the reproducible results.

For the CDS the asymmetry is lower than for the CHS at the same temperatures. The asymmetry temperature dependence for the CDS is similar to the CHS one.

Final Remarks

Due to high throughoutput of the pulsed muon channel at the ISIS pulsed source one gets the possibility of measuring the low damping rate and asymmetry. Thus it was possible for the first time to observe spasmodic changes of these values at the superionic phase transition. A comparison of our SR results with NMR data/9/ gives an additional argument that high ionic conductivity in CHS is the result of high mobility of protons in a superionic phase.

It seems interesting to perform model calculations of muon diffusion in such crystals to obtain exact positions of muons in the lattice and quantitative characteristic of diffusion parameters and compare them with the results obtained for protons. It is also interesting to verify the uniformity of the observed effects on other superionic conductors with hydrogen bounds.

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