Muons and muonium in Zn-spinels

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We have studied the magnetic spinel $(Zn)[Fe_2]O_4$ ($T_N \approx 10.5$ K) and the non-magnetic spinels $(Zn)[Al_2]O_4$, $(Zn)[Ga_2]O_4$, $(Zn)[ZnTi]O_4$ and $(Zn)[ZnSn]O_4$, both with surface and decay channel muons. In $(Zn)[Fe_2]O_4$ the relaxation rate increases monotonically from room temperature down, typical for a paramagnet. Around 30 K, an additional, stronger damped signal appears which is the signature of short-range ordered (SRO) regions. Their total volume fraction increases drastically towards T_N (reaching 75%) and astonishingly, continues to be present also below T_N where the rest of the material has become long-range ordered. Longitudinal field μSR proves the SRO to be dynamic. In $(Zn)[Al_2]O_4$ and $(Zn)[Ga_2]O_4$ muon depolarization is caused solely by ^{27}Al or $^{69,71}Ga$ nuclear dipoles. In the inverse spinel $(Zn)[ZnTi]O_4$, half of the implanted muons depolarize rapidly ($\lambda \approx 3$ μs^{-1} at room temperature). This, together with repolarization behavior in longitudinal fields indicates that the muon in $(Zn)[ZnTi]O_4$ undergoes a chemical reaction after implantation forming muonium. The fact that no such muonium formation occurred in another inverse spinel $((Zn)[ZnSn]O_4)$ means that the presence of muonium is not connected to the inverse structure but rather due to the presence of Ti which offers two d-electrons to participate in the chemical bonding. Additional evidence for d-electron participation is provided by ^{67}Zn-Mössbauer data which indicate unusual electron densities at the ^{67}Zn nuclei only in $(Zn)[ZnTi]O_4$.

1. Introduction

The spinels comprise an important class of compounds with a large variety of electronic properties: some spinels are superconductors with a relatively high transition temperature [1,2], others exhibit magnetic properties which make these systems interesting for magnetic storage devices and other technological applications [3]. Spinels crystallize in a face-centered cubic lattice with eight formula units in the cubic unit cell. Two basic types of spinels can be distinguished, the normal and inverse spinels. The *normal* oxide spinels can be described by the formula $(A)[B_2]O_4$ where A and B usually denote divalent and trivalent cations. The A site is tetrahedrally, the B site

octahedrally coordinated by oxygens. In the ideal spinel structure, the oxygen anions form a cubic close packed sublattice with the "oxygen parameter" $u = 3/8 = 0.375$. However, in most spinels $u \neq 0.375$ which leads to a trigonal distortion along [111] of the octahedron of oxygens surrounding the B site while the A site remains in cubic symmetry. *Inverse* spinels can be described by the formula (X)[YX]O$_4$. The X and Y metal ions occupy the B site in equal proportions. There exist also mixtures of normal and inverse structures.

We have studied the magnetic spinel (Zn)[Fe$_2$]O$_4$, the non-magnetic spinels (Zn)[Al$_2$]O$_4$ and (Zn)[Ga$_2$]O$_4$, and the completely inverted non-magnetic spinels (Zn)[ZnTi]O$_4$ and (Zn)[ZnSn]O$_4$ with μSR, neutron diffraction, and Mössbauer spectroscopy. In this paper the results of the μSR experiments are summarized and connected to the other data.

2. Experimental

The (Zn)[Fe$_2$]O$_4$ sample was prepared by heating in air thoroughly mixed powders of ZnO and Fe$_2$O$_3$. Details are provided in [4,5]. Neutron diffraction proved that inversion in this sample is less than 1%. The samples (Zn)[Al$_2$]O$_4$, (Zn)[Ga$_2$]O$_4$, (Zn)[ZnTi]O$_4$ and (Zn)[ZnSn]O$_4$ were prepared using similar procedures.

The μSR measurements were performed at PSI (decay channel muons) and TRI-UMF (surface muons) over a temperature range from 300 K to 1 K in zero, transverse and longitudinal magnetic fields up to 0.4 Tesla.

3. Results and discussion

3.1. The magnetic spinel (Zn)[Fe$_2$]O$_4$

The temperature dependence of the zero field muon relaxation rates is summarized in fig. 1. For $T \geqslant 4T_N$ ($T_N = 10.5$ K), the μSR spectra can be described by a single exponentially decaying signal with rate λ_1 which rises continuously as temperature is lowered. The temperature dependence of λ_1 is characterized by a power law $\lambda_1(T) \propto (T - T_N)^{-x}$ with $x \approx 0.4$. Such an exponent has been found in other critical experiments on magnetic materials using nuclear techniques [6]. Below ≈ 30 K a proper description of the μSR spectra needs a second exponentially decaying signal with $\lambda_2 > \lambda_1$. At this temperature one finds in addition that the exponent x of $\lambda_1(T)$ increases to $x \approx 0.6$ (see fig. 1). This is unusual. It probably signals that even in the regions which remain paramagnetic, spin correlations are enhanced. The relaxation rate λ_2 also first rises rapidly with reduced temperature, goes through a maximum at T_N and then decreases.

As mentioned, below ≈ 30 K in the μSR spectra two signals characterized by λ_1 and λ_2 are observed (see fig. 1). As fig. 2 demonstrates, the volume fraction of the fast
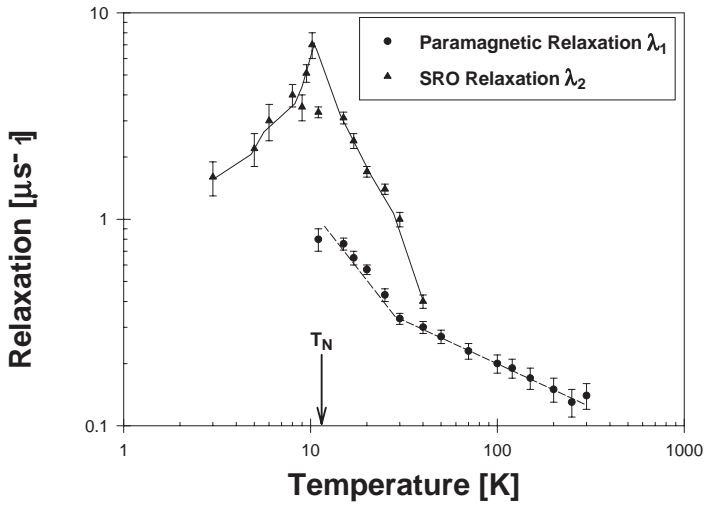
Fig. 1. Temperature dependence of the paramagnetic (λ_1) and the short-range order (λ_2) relaxation rate in (Zn)[Fe$_2$]O$_4$. The broken lines through the data points of λ_1 represent straight-line fits. The solid line through the data points of λ_2 is just a guide to the eye.
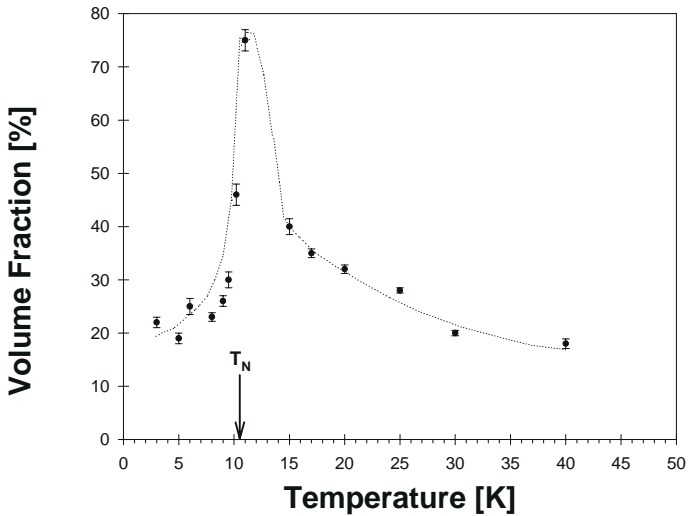

Fig. 2. Volume fraction of the short-range ordered regions in (Zn)[Fe$_2$]O$_4$ as function of temperature. The dashed line is a guide to the eye only.

decaying portion (λ_2) increases sharply when approaching T_N from above and reaches $\approx 75\%$ at T_N. For $T < T_N$ the signal λ_1 is lost, meaning that now $\lambda_1 \geqslant 100 \ \mu s^{-1}$, while the signal λ_2 remains visible with, however, rapidly decreasing volume fraction which reaches a limiting magnitude of $\approx 20\%$ at 3 K. These volume fractions are in close agreement with the corresponding values derived from our neutron diffraction

experiments on the identical sample [4,5]. Above $\approx$ 40 K the μSR spectra are no longer sensitive to an analysis using two signals.

In accordance with the neutron data we interpret signal λ_1 in the regime $T \geqslant T_N$ as arising from a regular paramagnetic fraction. It enters long-range antiferromagnetic order at T_N. The signal λ_2 is the signature of the presence of a short-range ordered fraction. The unusual result is, that this fraction appears already well above T_N and persists in the presence of long-range magnetic order even well below T_N. As a consequence, even at 4.2 K (Zn)[Fe$_2$]O$_4$ is not fully long-range ordered throughout its bulk. The damping rate λ_2 cannot be influenced by a longitudinal magnetic field. At most, λ_2 drops $\approx$ 5% at 0.4 T, from which we estimate that the fluctuation rate must be above 1.5 GHz. This means that the short-range order is of dynamic nature.

In summary, these results show that (Zn)[Fe$_2$]O$_4$ is a superantiferromagnet exhibiting short-range magnetic order far above T_N. Below T_N short- and long-range magnetic order coexist, the short-range order losing intensity in favor of the long-range order. At 4.2 K still $\approx$ 20% of the sample remain short-range ordered. Further details are given in [4] and [5].

3.2. The non-magnetic normal spinels (Zn)[Al$_2$]O$_4$, (Zn)[Ga$_2$]O$_4$

The zero field muon depolarization rates of (Zn)[Al$_2$]O$_4$ and (Zn)[Ga$_2$]O$_4$ are temperature independent and can easily be decoupled in small longitudinal fields. The depolarization rates are of the order of 0.1 μs^{-1} and arise from the interaction with ^{27}Al or ^{69,71}Ga nuclear dipoles.

3.3. The non-magnetic inverse spinels (Zn)[ZnTi]O$_4$, (Zn)[ZnSn]O$_4$

The results for the inverse spinel (Zn)[ZnTi]O$_4$ are quite different. In the zero field spectra we observed a rapidly damped signal ($\lambda \approx$ 3 μs^{-1}) at room temperature and below, affecting $\approx$ 50% of the implanted muons (fig. 3, top). In longitudinal fields up to 0.38 T, the depolarization rate could be weakened (fig. 3, bottom).

To see whether the unexpected behavior is related to the inversion present in (Zn)[ZnTi]O$_4$, we performed experiments on another inverse spinel, (Zn)[ZnSn]O$_4$. In this material we did not observe the strong damping found in (Zn)[ZnTi]O$_4$. (Zn)[ZnSn]O$_4$ behaves as expected for a diamagnetic compound.

The strong damping belonging to $\approx$ 50% of the implanted muons in (Zn)[ZnTi]O$_4$ cannot be caused by magnetic interactions. The material is diamagnetic and the nuclear magnetic moments of the constituents are zero or very small in the natural isotopic average. The most likely explanation is the formation of muonium. At $t \to 0$ the full initial asymmetry is observed. This means that all muons are initially stopped as μ$^+$ but within less than 1 μs an electron (most likely from the oxygen bond) is captured to form muonium. The reduced damping rate exhibited in the 0.38 T longitudinal spectra can be explained when a repolarization of 40% is assumed. This model fits the data for $T \geqslant$ 200 K well. An example are the lines through the data points in
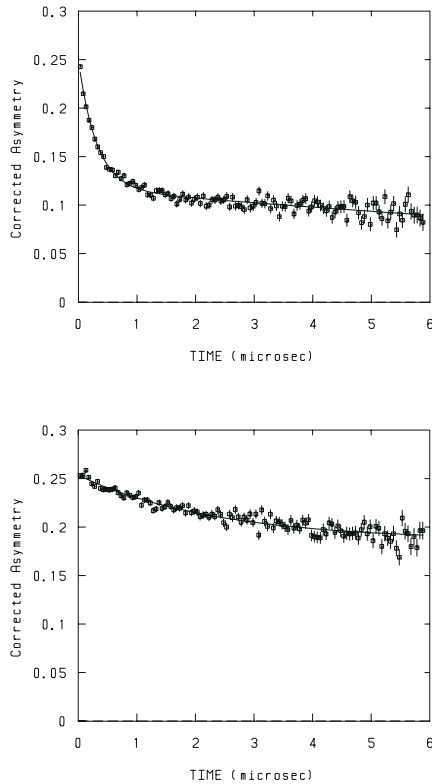
Fig. 3. μSR-spectra of $(Zn)[ZnTi]O_4$ at 250 K in zero field (top) and 0.38 T longitudinal field (bottom).

fig. 3. At lower temperatures the initial decay of polarization becomes more complex and needs more than one component for a proper description. This point needs further work.

We did not see any evidence for muonium formation in the other three non-magnetic spinels investigated. Therefore muonium formation can neither be a general property of non-magnetic spinels nor is it related to inversion. It is rather an intrinsic property of $(Zn)[ZnTi]O_4$. Most probably it is connected with the presence of Ti, which offers two d-electrons to participate in the chemical bonding. Additional evidence for d-electron participation is provided by ^{67}Zn-Mössbauer results which indicate unusual electron densities at the ^{67}Zn nuclei only in $(Zn)[ZnTi]O_4$.

Acknowledgements

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