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Muon diffusion in intermetallic compounds of the $MoSi_2$-type structure

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Abstract

The localization and diffusion of positive muons are studied in three binary metallic systems, Zr_2Cu, Hf_2Cu and Ti_2Cu, presenting the $MoSi_2$-type structure. Zero-field μSR measurements are interpreted as the muons being static in the T_b/O_b interstitial site at low temperatures and, as the temperature is increased, starting diffusing through the network of T_b sites around the O_b site, until they reach a state occupying simultaneously the four T_b sites. Long-range diffusion is observed above 300 K. Activation energies for the lower-temperature diffusion processes are obtained. The results are interpreted in terms of the lattice structure characteristics.

1. Introduction

Detailed information on the static and dynamic properties of muons, as interstitial particles in materials, can be obtained by μ^+SR spectroscopy [1]. Muons are sensitive to the magnitude, symmetry and fluctuations of local surrounding magnetic fields, yielding information on the environment where they are located. Positive muons are in many aspects similar to protons and therefore valuable information on the static behaviour of hydrogen in materials can be deduced by this method. Muon diffusion parameters, although not immediately transferable to the hydrogen case, provide information useful for the study of hydrogen diffusion processes [2, 3].

This work is part of a study of positive muon diffusion and localization in binary alloys embracing the study of its crystal structure dependence for the same elemental composition and its dependence on the elemental composition for the same structure. The work presented in this paper consists of the study by μ^+SR spectroscopy of the behaviour of implanted muons in a series of binary alloys presenting the same $MoSi_2$ crystallographic structure. The alloys under study were Zr_2Cu, Hf_2Cu and Ti_2Cu. They crystallize in the tetragonal $MoSi_2$-type structure belonging to the $I4/mmm$ space group. Cu occupies the 2a (0, 0, 0) position and Zr (Hf or Ti) occupies the 4e (0, 0, z) position as shown in figure 1.

2. Experimental details and results

Polycrystalline samples were prepared from high purity elements by HF melting under an argon atmosphere. X-ray diffraction using a high resolution transmission diffractometer was

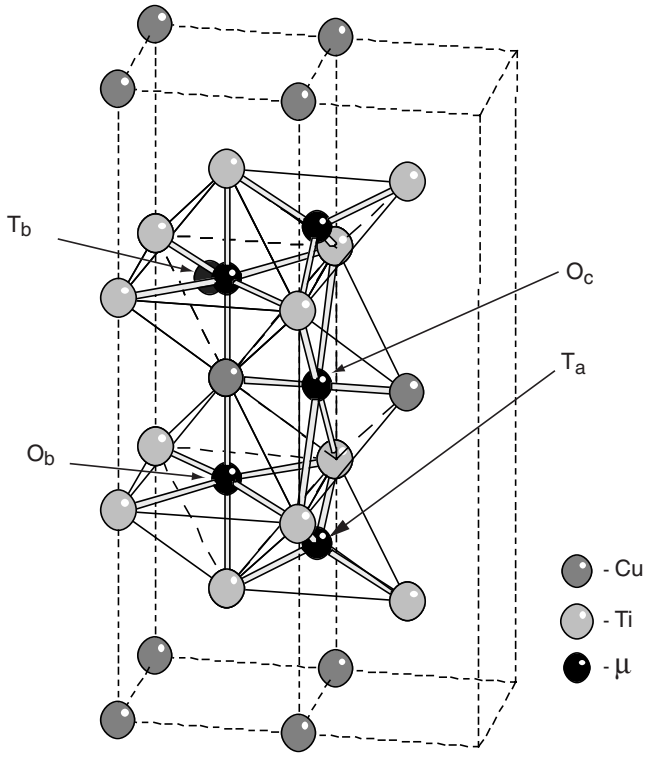

Figure 1. Tetragonal unit cell of the $MoSi_2$-type structure, showing some of the interstitial sites available for the muon. There are four T_b sites surrounding each O_b site.

Table 1. Lattice parameters, z coordinate and unit cell volume for Zr_2Cu, Hf_2Cu and Ti_2Cu.

Sample	a (Å)	c (Å)	z (Å)	Unit cell volume (Å^3)
Zr_2Cu	3.218 (1)	11.186 (1)	0.3456 (1)	115.9
Hf_2Cu	3.168 (1)	11.137 (1)	0.3449 (2)	111.8
Ti_2Cu	2.935 (2)	10.772 (2)	0.3320 (9)	92.8

used to verify the crystallographic structures. In all samples we obtained virtually 100% of the desired tetragonal phase. (A typical x-ray spectrum, obtained for Zr_2Cu, is shown in figure 2.) The lattice parameters and the parameter z for the 4e position were obtained for all the samples. The refinement used the Rietveld method and the Fullprof program [4]. The results are presented in table 1.

μ^+SR measurements were carried out in zero applied field and longitudinal geometry using the ISIS pulsed muon source at the Rutherford Appleton Laboratory, UK (EMU and MuSR lines). The alloys were reduced to powder and circular samples with 20 mm diameter and 1 mm thickness were prepared. Measurements were carried out in a temperature range from 15 K to 330 K. The background signal, originated from muons stopped in the sample environment, was determined using an $ErAl_2$ sample in a transverse-field measurement at 20 G [5]. Typical zero-field μ^+SR spectra at different temperatures for Zr_2Cu are illustrated in figure 3.

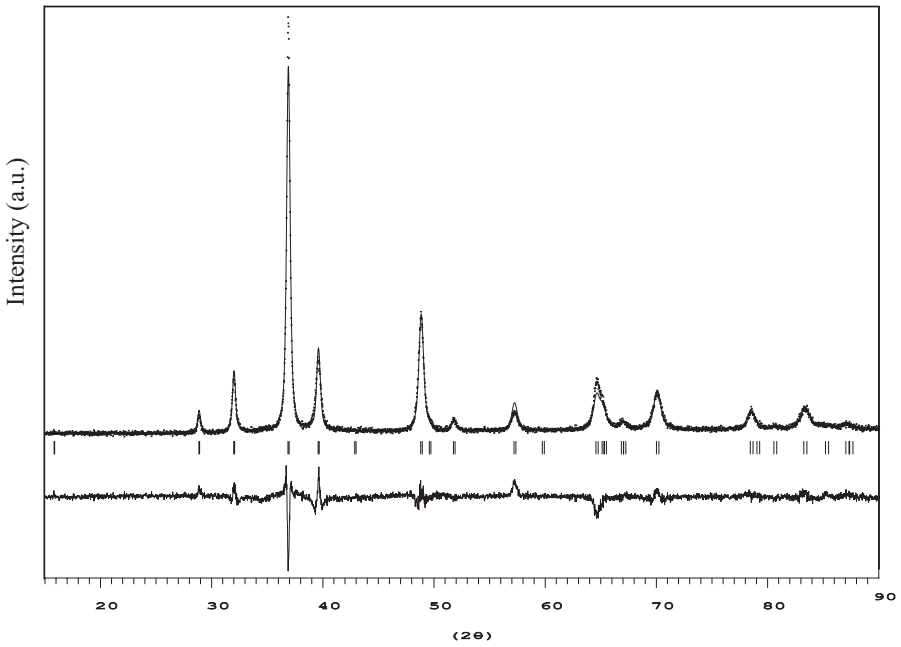

Figure 2. Experimental (dots) and calculated (lines) x-ray diffraction patterns for Zr_2Cu. The difference pattern (observed − calculated) is shown at the bottom of the figure.

3. Analysis and discussion

3.1. Preliminary analysis

A series of fits to the experimental data using a single static Kubo–Toyabe (K–T) function [6, 7]

$$P_z(t) = \tfrac{1}{3} + \tfrac{2}{3}(1 - \Delta^2 t^2)\exp(-\tfrac{1}{2}\Delta^2 t^2) \tag{1}$$

was first considered. In this equation, z is the direction of the initial muon spin polarization, coincident with the beam direction in the longitudinal geometry set-up, and Δ is the width of the isotropic Gaussian distribution of the local magnetic fields, which are considered to be static and random. The $1/3$ term corresponds to the fraction of muons that are at positions where the local field is aligned either parallel or antiparallel to the initial spin polarization, while the remaining $2/3$ of the spin polarization precesses due to the transverse local field components.

The Δ values obtained from the fits are presented in figure 4 as a function of temperature. For all compounds, three distinct regions can be identified: one, at low temperatures, showing a plateau in the value of Δ; another, where Δ decreases with increasing temperature; and a third region, where Δ seems to attain a new plateau with a lower Δ. In Zr_2Cu, a new decrease of Δ can be guessed from the value at the highest temperature. The average values of Δ in the first (Δ_1) and the third (Δ_2) region of temperature plateaus are presented in the first columns of table 2.

A first possible interpretation is as follows. The muon is static at low temperatures, the Δ_1 values characterizing the local nuclear fields experienced by the muon in the occupied sites. The decrease of Δ observed in the second region corresponds to motional narrowing, indicating muon diffusion. If long-range diffusion takes place, it is expected that the muon

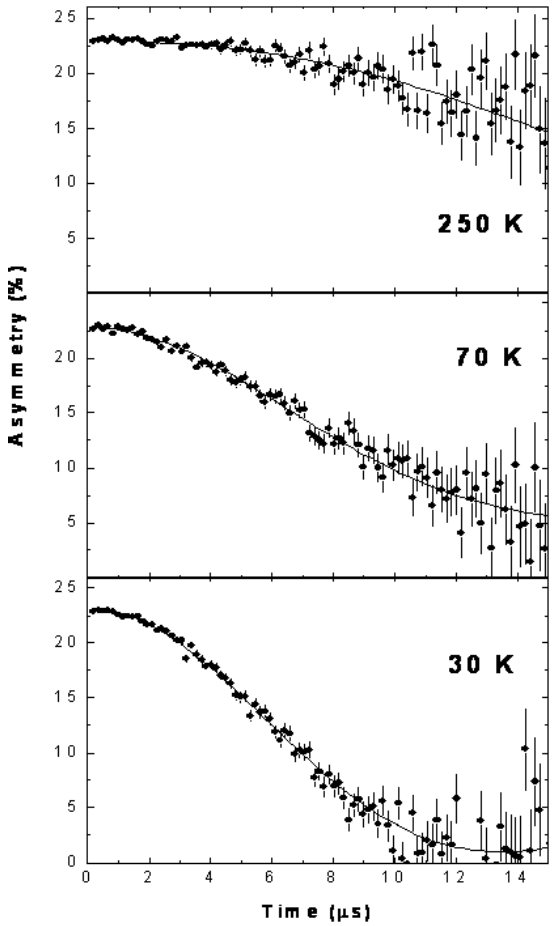

Figure 3. μ^+ decay asymmetry obtained for Zr_2Cu in zero applied field, at different temperatures. The solid lines are fits using the function in equation (2).

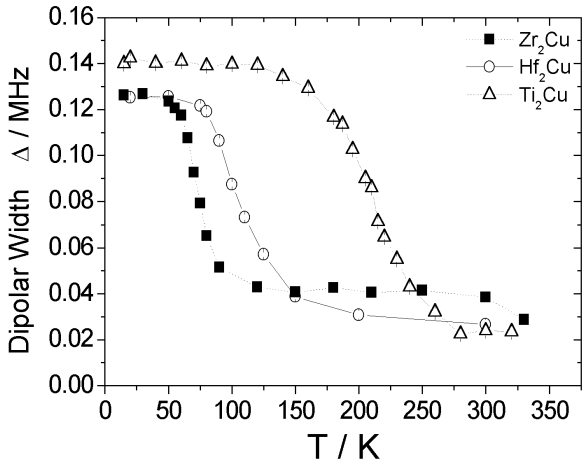

Figure 4. Width Δ of the local field distribution as a function of temperature for the three samples. The lines are only guides to the eye.

Table 2. Width of the distribution (MHz) of the static dipolar fields in the Van Vleck limit, calculated at different interstitial positions available for the muon in the $MoSi_2$-type structure. Extracted from figure 4 and shown for comparison are: Δ_1—plateau values of Δ (MHz) at low temperatures for the three samples; Δ_2—plateau values of Δ (MHz) at high temperatures. In the first row, the numbers in parenthesis correspond to the number of interstitial sites by formula unit.

Sample	Δ_1	Δ_2	(2) O_a	(4) O_b	(4) O_c	(4) T_a	(16) T_b	(8) T_c
Zr_2Cu	0.127(1)	0.041(2)	0.139	0.152	0.276	0.056	0.148	0.191
Hf_2Cu	0.125(1)	0.027(2)	0.145	0.147	0.290	0.058	0.148	0.198
Ti_2Cu	0.140(1)	0.023(2)	0.183	0.172	0.364	0.068	0.166	0.261

does not stop in any specific site and so the motional narrowing should continue until a zero mean value is reached. The observation of a plateau in the third temperature region can be interpreted as the muons being stopped at a different site, characterized by the Δ_2 values. A second diffusion process from the latter sites would explain the decrease in Δ above 300 K for Zr_2Cu.

3.2. Muon sites in the $MoSi_2$ structure

Assuming that the muons are static at the high and low temperature plateaus an identification of the occupied sites was tried by a careful study of the interstitial sites available for the muon in the lattice followed by calculations of the corresponding depolarization rates expected in the Van Vleck limit.

In figure 1, some of the interstitial sites available for muon occupation in the $MoSi_2$ type structure are shown. Due to their large size and strong electronic affinity for hydrogen isotopes, three octahedral sites—O_a, O_b and O_c, coordinated, respectively, by (4 Cu, 2 Zr), (1 Cu, 5 Zr) and (2 Cu, 4 Zr)—and three tetrahedral sites—T_a, T_b and T_c, coordinated, respectively, by (4 Zr), (1 Cu, 3 Zr) and (2 Cu, 2 Zr) were considered.

Using the Van Vleck approximation for non-identical spins [8], it is possible to calculate the second moment of the local magnetic field distribution created by the surrounding nuclear magnetic moments at each interstitial site. The zero-field dipolar width Δ is directly derived from this second moment. Calculations were carried out using the positions of the Zr (Hf or Ti) and Cu atoms found on the x-ray analysis and introducing nuclear magnetic moments on the Cu atoms alone. This is justified by the fact that all Cu nuclei are magnetic (69% of ^{63}Cu have a nuclear moment of 2.22 μ_N and 31% of ^{65}Cu have a nuclear moment of 2.38 μ_N) [9]. On the other hand, most natural titanium, hafnium and zirconium nuclei are non-magnetic and those isotopes having a magnetic moment different from zero have very low abundances. The natural abundance of ^{91}Zr, that has the highest moment (-1.3 μ_N), is only 11%. It was calculated that even a contribution of 100% for this isotope would increase the Δ values by only less than 10%. The contribution of these nuclei was therefore neglected in our calculations.

Although the local lattice expansion due to the polaron effect seems difficult to evaluate, published results comparing theoretical and experimental Δ values [3, 10], have led us to consider a reduction of 20% on the calculated values of Δ. The results are shown in table 2.

3.3. Muon localization

Comparing the experimental Δ_1 values at low temperatures with the calculated values (table 2) a statistical distribution of the muons among the different interstitial sites [11] did not seem appropriate since the weighted average of the dipolar width of the available interstitial sites is 20% to 40% larger than the experimental values. According to the values presented in table 2

the most probable sites for muon occupancy are interstitials O_b and T_b. O_a sites present also a convenient Δ value in the case of Zr_2Cu and Hf_2Cu but its size is more than 50% smaller. Tetrahedral sites T_b, with three Zr (Hf or Ti) atoms as coordination, are the largest sites in the unit cell, and form closed and large paths around O_b. Good fits to the data are obtained at these low temperatures using a static Kubo–Toyabe function. We assume that the Δ plateaus correspond to muons static at the O_b or T_b sites. A potential reason for the difference between theoretical and experimental values of Δ is either a polaron effect more important than 20% or a higher order influence of additional interactions. One possibility would be the quadrupole interaction due to the electric field gradient produced by the muonic charge [12]. However, as in recent transverse field measurements in a different binary intermetallic compound, Ti_2Co, with fields up to 0.6 T no change of the dipolar linewidth could be detected, this possibility might not be appropriate.

To assign an interstitial site to the high temperature plateau with Δ_2 values, as presented in table 2, it is apparent that the closest calculated values are for the T_a site. Other interstitial positions, mainly or totally coordinated by Zr (Hf or Ti) atoms have a rather small size and the corresponding values of Δ are larger than the values found for sites T_a, and were therefore discarded. The site with the smallest calculated Δ is a substitutional position of Cu, a site with eight Zr atoms in the first neighbourhood. The Δ calculated for this position (including the polaron effect) was 0.054 MHz for Zr_2Cu, 0.057 MHz for Hf_2Cu and 0.071 MHz for Ti_2Cu. These values are very similar to those calculated for the interstitial site T_a. A discrepancy is found when noticing that the calculated Δ values increase for all considered sites from Zr to Ti, while the experimental Δ_2 values decrease.

This discrepancy indicates that the simple static muon interpretation presented for the low temperature case, does not apply in this case and a more complex muon behaviour has to be considered. This is presented below.

3.4. Muon diffusion

The above discussions suggest a reanalysis of the data considering the effect of muon motion on the spin depolarization.

The effects of muon diffusion are generally described within the framework of the strong collision model [6, 13]. The muon is assumed to occupy equivalent sites successively, jumping at random times with an average frequency ν_d. The time of a jump is taken to be much shorter than the mean residence time at one site. The model also assumes that there is no correlation between the local field experienced by the muon before and after the jump. The total depolarization function within this model (dynamic K–T function) can then be written as

$$G(t) = G(0,t)\exp(-\nu_d t) + \nu_d \int_0^t G(\nu_d, t'-t)\exp(-\nu_d t)G(0,t')\,\mathrm{d}t' \qquad (2)$$

where ν_d is the correlation frequency (or jump rate) characteristic of the fluctuations of the dipolar interaction between the diffusing muon and the surrounding nuclear magnetic moments, and $G(0,t)$ is the static depolarization function, in this case assumed to be the static Kubo–Toyabe formula (equation (1)).

The data were reanalysed using formula (2). Assuming that the muon diffuses through the sites characterized by a Δ_1 value, for each of the compounds the respective value was taken as a fixed parameter in the fitting at all temperatures.

The jump rates obtained are presented in figure 5 as Arrhenius plots. It is observed that for a certain temperature range depending on the compound the muon is involved in an activated diffusion process, the jump rates following an Arrhenius behaviour. This corresponds to the temperature ranges of motional narrowing in figure 4. The onset temperature of the motional

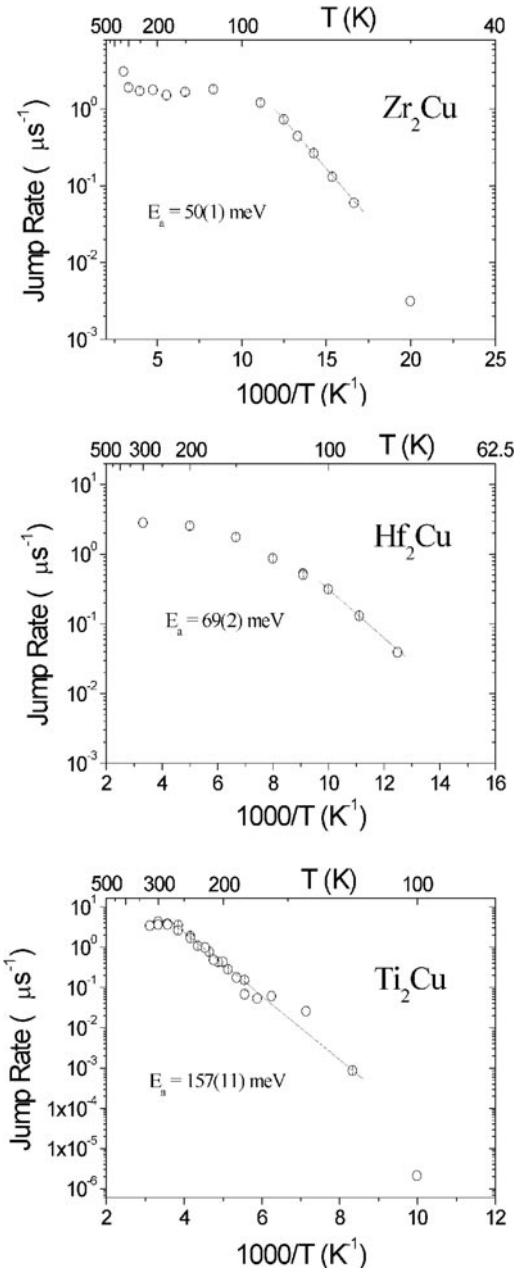

Figure 5. Arrhenius plots of the jump rate in Zr_2Cu, Hf_2Cu and Ti_2Cu. The lines are the results of fits of an exponential function yielding the indicated activation energies E_a.

narrowing is the lowest for Zr_2Cu, the compound with the highest unit cell volume, and much higher for Ti_2Cu (with the smaller unit cell—see table 1). This means that muons require less energy to move out of the T_b/O_b sites in the larger unit cells of Zr_2Cu and Hf_2Cu. Activation energies were drawn from fits to the pertaining experimental points in the Arrhenius plots: the values found were 50(1) meV for Zr_2Cu, 69(2) meV for Hf_2Cu, and 157(11) meV for

Ti_2Cu.

Above a temperature depending on the compound, the fitting procedure with fixed Δ_1 no longer gives a good description of the data, yielding a constant jump rate value, no longer following an Arrhenius behaviour. We conclude that the activated diffusion process is interrupted.

A trapping and detrapping mechanism due to impurities or structural defects, which would seem to be a plausible interpretation of this behaviour, was discarded for the following reason. The average distance travelled by the muons in these trapping situations (in the present case the muon jump rate being of the order of 1 μs^{-1} at the temperature considered) would imply a high concentration of defects, which is not the case in our samples.

Our interpretation is that the muon is thought to be static at T_b sites in the lower temperature range. At the onset of motional narrowing, the muon starts to diffuse within a local set of T_b sites (the four equivalent sites around an O_b site), in an activated diffusion process. Muons cannot leave the O_b cage due to the high barrier for jumping into the T_a sites, which are the next neighbouring sites with the highest probability of occupation due to the proximity (they share faces with T_b/O_b) and electronic affinity to the muon. The diffusion through the identical T_b sites implies a depolarization that should be well fitted with a dynamical K–T function, and that was confirmed. This type of localized motion has already been observed for hydrogen in intermetallic C15-type Laves phases using NMR and QNS [14, 15].

With increasing temperature, the muon acquires enough energy to be insensitive to the potential barriers within the cage, its wavefunction occupying the four T_b sites and the O_b site as well. The depolarization function is then equivalent to that of a static muon with a Δ value lower than the values calculated for the single sites [16, 17], as was indeed found in the preliminary analysis for the highest temperature plateaus (figure 4).

The mentioned barrier to jump to the T_a sites would be overcome at higher temperatures, starting a process of long-range diffusion. Such behaviour seems to be perceived in the cases of Zr_2Cu and Hf_2Cu. Actually, a small dynamic contribution (ν_d) was detected at the highest temperature: 330 K for Zr_2Cu and 300 K for Hf_2Cu, in fits with a dynamic K–T function with Δ_2 as dipolar width.

4. Conclusions

The results obtained for muon localization and diffusion in Zr_2Cu, Hf_2Cu and Ti_2Cu suggest that the muon occupies a T_b or O_b site at low temperatures.

In the motional narrowing regime, the muon performs a short-range diffusion within the network of T_b sites. From the Arrhenius behaviour of the jump rate with temperature, the activation energies which characterize this process have been estimated for each compound. From the results and from the temperature at which diffusion sets in, it can be deduced that this activated diffusion process requires less energy in the larger unit cells.

A third regime is observed in these compounds when the jump rate increases to about 1 μs^{-1}. The activated diffusion process is interrupted when the muon has enough energy to occupy simultaneously the four T_b sites in the O_b network. This behaviour is similar to a trapping process, but without diffusion to a long distance from the original site. Long-range diffusion is perceived only at temperatures above 300 K.

The μ^+SR results presented in this work suggest that structural reasons, in this case the different size of the atoms Zr, Hf and Ti and the consequent differences in the cell volumes, are responsible for the different muon behaviour observed in the three alloys under study.

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