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LETTER TO THE EDITOR

Muon spin relaxation investigation of the 9R-related phase change in lithium and sodium

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Abstract. Lithium and sodium have been studied by the muon spin relaxation technique. When cooling the lithium, the 9R-related phase was first observed at 73 K, below 50 K this environment was the dominant one for the muons. In sodium, evidence was found that a significant part of the sample was in the 9R-related phase at 45 K. In both samples the muons diffused rapidly in the BCC phase, and in lithium they were clearly static in the 9R phase below 20 K.

The transformation of lithium and sodium from the BCC phase to a 9R-related phase is of great topical interest. Studies of the evolution of this phase change have been carried out by neutron diffraction and the transformation temperature has been reported to be about 77 K and 35 K in lithium and sodium respectively (Berliner *et al* 1989). In lithium the 9R-related phase co-exists with the BCC phase and traces of FCC at 20 K. At the same temperature sodium showed evidence of a small fraction of HCP phase in addition to the BCC and 9R-related phases.

The 9R-related phase is a close-packed structure with a stacking sequence of nine layers. The 9R-related phase transition involves a distortion of the (110) planes of the BCC lattice (figure 1) acompanied by a modulated shearing motion parallel to them that is not shown here (Wilson and de Podesta 1986, Gooding and Krumhansl 1988). In lithium the transition is accompanied by a volume expansion of 0.09% whilst the volume change reported for sodium has the higher value of 0.3% (Berliner *et al* 1989). A martensitic transformation has also been observed in rubidium (Templeton 1982), but the transition temperature is low.

Muon spin relaxation spectroscopy is particularly well suited for studies involving localized changes within a sample. The assignment of peaks when performing neutron diffraction experiments to the different phases of relevance here demands high resolution to avoid complications from the overlap of reflections. To muons, the difference between phases can be perspicuous as, being an interstitial particle probe, they are extremely sensitive to changes in the local environment.

Little is known about hydrogen diffusion in either lithium or sodium, making welcome any information obtained about diffusion. Indeed, BCC structures are, in general, less accessible to diffusion studies using the muon spin relaxation technique than FCC

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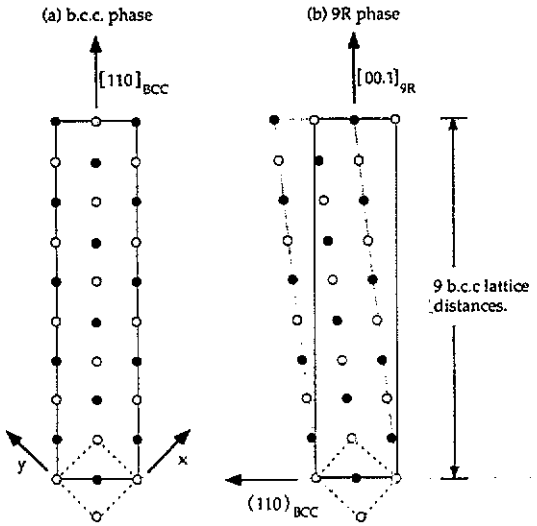

Figure 1. The relationship between the structure of the BCC phase and the 9R phase. The (110) is sheared and undergoes a modulated displacement (not shown). The open circles represent atoms at $z = 0$ and the full circles those at $z = \pm\frac{1}{2}$.

ones. This is due to diffusion taking place too rapidly in BCC metals for facile measurement. The muon is generally considered to occupy the same sites as hydrogen which, at low concentrations, is a tetrahedral interstitial site in BCC metals.

The lithium sample consisted of pure (99.95 wt.%) isotope separated (99.98 at.%) ^{7}Li. The sodium was 99.95% pure. These samples were sealed into aluminium containers, the lids of which were sufficiently thin not to stop a significant proportion of the muon beam.

The muon is essentially a light isotope of hydrogen. The mass of a muon is 0.11 times that of a proton, it has a spin of one half and is positively charged. By implanting spin polarized muons and monitoring their subsequent decay into a positron plus neutrinos, the immediate environment of the muon may be probed. The positrons are emitted with a strong preference for the direction in which the spins of the muons point at the instant of decay. During the lifetime of a muon its spin couples to the spins of unpaired electrons or to nuclear spins, which leads to a modulation of the average muon polarization and of the observed asymmetry in the spectra: $a(t) = a(0)\, G_z(t)$ where $a(0)$ corresponds to the observed initial asymmetry.

In the analysis of zero-field muon spin relaxation data, completely static muons are described by a Kubo–Toyabe relaxation function (Kubo and Toyabe 1967) characterized by the dipolar width Δ_0

$$G_z(t) = \tfrac{1}{3} + \tfrac{2}{3}(1 - \Delta_0^2 t^2) \exp(-\tfrac{1}{2}\Delta_0^2 t^2).$$

If the muons diffuse with a characteristic jump time, τ_c, then the dynamic depolarization function is already known (Hayano *et al* 1979), again characterized by the width Δ_0 and also by the time τ_c. For fast diffusion the spectra are undepolarized.

At the Rutherford Appleton Laboratory, the accelerator for the spallation neutron source is used to produce intense pulses of polarized muons. This enables muon spin relaxation spectra to be collected with a low background, and thus allows significant statistics to be obtained even at long times within a reasonable measurement period.

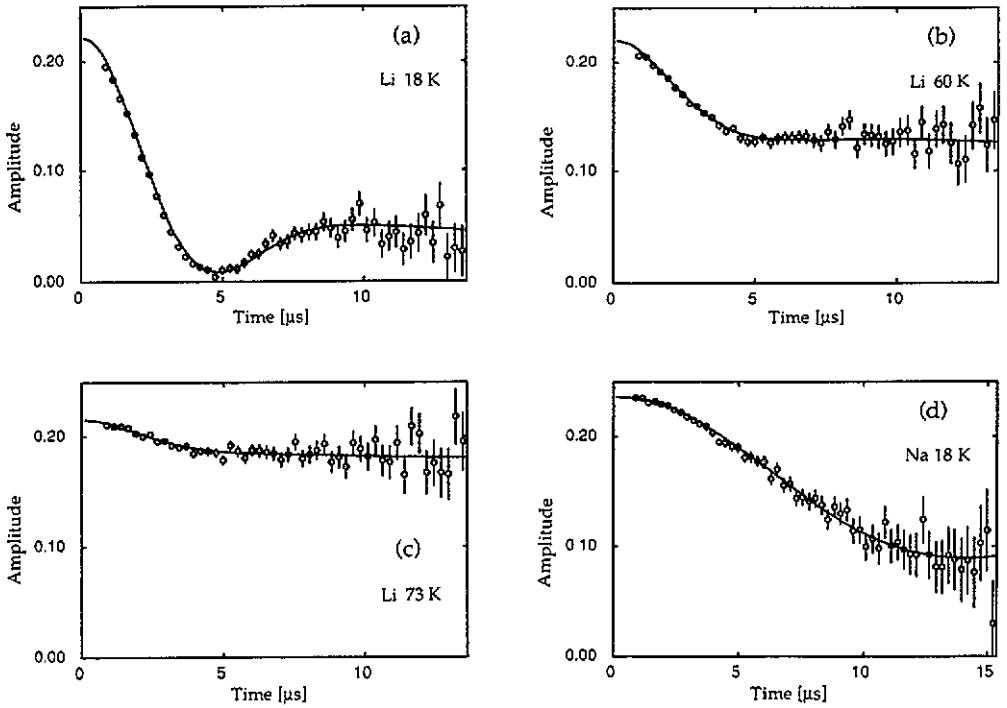

Figure 2. Experimental muon spin relaxation spectra: (*a*) lithium at 18 K; (*b*) lithium in the temperature regime with coexisting phases; (*c*) lithium at the transition temperature; (*d*) sodium at 18 K.

Thus low depolarization rates may be measured and small changes can be observed when the temperature is scanned.

The experiments were performed for (i) lithium and (ii) sodium in a compensated zero field and the absolute value of the initial asymmetry was found from measurements in a transverse field.

The muon spin relaxation data for lithium, of which typical spectra are displayed in figure 2, is best fit with just one non-depolarized component from room temperature down to 96 K. The absence of depolarization in this temperature interval indicates that the muon is diffusing rapidly. At 73 K it was obvious from the spectra (see figure 2(*c*)) that an additional, and depolarized, component was needed. This corresponds to the appearance of the 9R-related phase. As the temperature was further decreased, it was seen that this fraction grew until, at about 30 K, the data is again best fit with just one component. Only the 9R-related phase appears to be present below this temperature; the spectra displayed in figures 2(*a*) and 2(*b*) are from 18 K and 60 K, respectively. The former of these figures is from the lowest measured temperature whilst the latter is from the regime in which two phases are present in the sample.

The experimental value obtained for the low temperature width, Δ_0, was 0.41 μs^{-1}. This is somewhat higher than the value of 0.33 μs^{-1} calculated for static muons depolarizing in the BCC phase. A minimum in the depolarization rate at about 5 μs is evident followed by a recovery at long times (figure 2(*a*)). However, it was noted that a complete

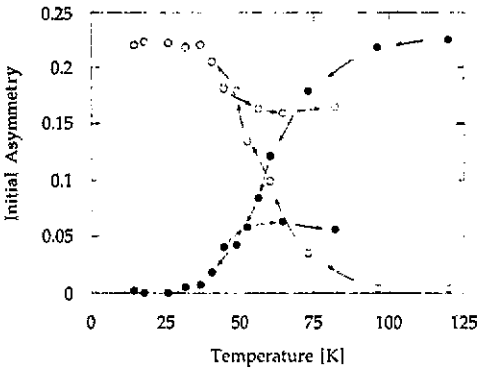

Figure 3. The initial asymmetry of the two components for lithium. ●: the fraction of the muons in the BCC phase; ○: the fraction stopped in the 9R-related phase.

recovery to one third of the total initial asymmetry was not observed. Nevertheless, the distinct minimum and ensuing recovery indicate that the muons were indeed static.

Above 20 K, the recovery was no longer well defined although it was still distinguishable at 55 K, this implies that the muons are partially mobile at this temperature in the 9R phase. The data were fitted with a dynamic Hayano function (Hayano *et al* 1979) which takes slow diffusion into account. The static width 0.41 μs^{-1} was found to fit the 9R phase throughout the temperature range. It should be noted that in the analysis, the depolarization rate is taken to be zero in the BCC phase corresponding to rapid diffusion, which is evidently the case down to at least 73 K. Below this temperature, the justification for fixing the depolarization rate at zero arises from the knowledge that diffusion in pure BCC metals is known to be fast, e.g. Fe and Nb (Seeger 1984).

The initial asymmetry of the two components is plotted as a function of temperature in figure 3 and corresponds physically to the relative numbers of muons stopping in each phase. On cooling the lithium, only one phase was observed at 96 K, but a second component had appeared by 73 K indicating that the transition temperature lies in this interval. A marked hysteresis effect is evident whereby the data recorded whilst decreasing and increasing the temperature, differ substantially. This is in agreement with neutron scattering (Smith 1987). Our results are compatible with estimates that the sample consisted of equal amounts of the two phases at approximately 60 K.

By 30 K all the muons were static in the 9R-related phase. This implies that regions of the BCC phase could still exist in the lithium, but, were that the case, they would be so small that the muons may readily diffuse from them within a fraction of a microsecond after implantation. Neutron measurements at 20 K (Berliner *et al* 1989) found that only 66% of the sample had converted to the 9R phase. Upon warming, the lithium was found to gradually resume the BCC structure with about 10% of the sample being in the BCC phase at 41 K and 25% by 82 K.

The analysis of the sodium data is complicated by the fact that the depolarization rate is lower making it difficult to determine whether the muons are static or not at low temperatures. The spectrum obtained at the lowest temperature for sodium is shown in figure 2(*d*). The sodium spectra, like those of lithium, required two components to fit the data, one of which was undepolarized corresponding to muons diffusing rapidly in the BCC phase. The other component was best fit throughout the temperature range by

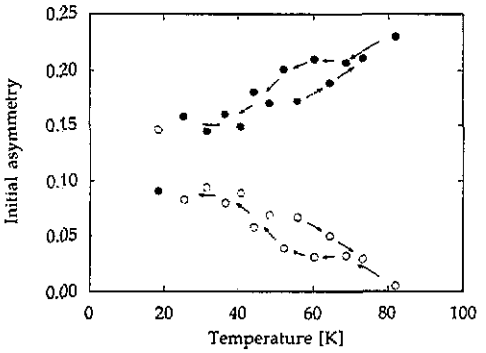

Figure 4. The initial asymmetry of the two components for sodium. ●: the fraction of the muons in the BCC phase; ○: the fraction stopped in the 9R-related phase.

using a trapping function of the type used by Petzinger (1980) with a fixed width indicating some mobility prior to trapping in the 9R phase. It was, however, difficult to determine the absolute value of Δ_0 as, to some extent, a change in the depolarization rate when fitting with a trapping function is compensated by a change in the trapping rate. The static width certainly lies close to the calculated value of 0.137 μs^{-1} for muons in the BCC lattice. The initial asymmetry is almost independent of the depolarization rate where small changes are concerned.

The initial asymmetry of the muons is plotted as a function of temperature in figure 4. It is deduced from this that there is already a significant fraction of the sodium in the 9R phase just below 50 K, which would indicate that the phase transition takes place at higher temperatures than the 35 K measured by neutron scattering. The lowest temperature spectrum, 18 K, has a much increased depolarization rate that probably reflects some trapping in the BCC phase rather than a rapid acceleration in the phase transition. At 25 K about 40% of the sodium has transformed from the BCC phase in accordance with the 43% measured at 20 K by Berliner *et al* (1989).

The presence of a small depolarized fraction above 50 K is probably an artifact of the rapid diffusion of muons in the BCC phase and their subsequent trapping at impurities. This disappears at higher temperatures as the muons have sufficient energy to escape from the traps.

The function required to fit the depolarizing contribution of the spectra indicates that the mobility is high enough for the muon to diffuse to a trap in the 9R phase within its lifetime. The fact that the shape of the lithium and sodium spectra differ may reflect a difference in purity between the samples, and points to more rapid diffusion in BCC sodium. It should also be noted that the transitions in sodium and lithium differ. Below the transition temperature, traces of HCP are observed in sodium (Berliner *et al* 1989) whilst in lithium small amounts of FCC have been observed in pressure measurements. Furthermore, pressure experiments reveal that whilst the transition temperature for lithium increases with the application of pressure (Smith *et al* 1990), in sodium the opposite is observed (Smith *et al* 1991).

Muon spin relaxation has been used to follow the evolution of the 9R-related phase in lithium and sodium. As the muons appear to diffuse rapidly in the BCC phase and be only partly mobile in the 9R phase the contributions from the two phases differ strongly.

Thus muon spin relaxation becomes a powerful tool for the examination of this phase transition. In lithium, evidence was found of a small percentage of 9R phase at 73 K. In addition to this, it was observed that muons diffuse rapidly in the BCC phase at least down to 73 K. At low temperatures no evidence was found for the existence of the BCC phase indicating that either all the sample was in the 9R phase or that the quantity and size of the BCC regions were such that the muons were able to diffuse into the 9R phase within a fraction of a microsecond of implantation. The shape of the spectra revealed that muons are static below 20 K in lithium in the 9R phase.

In sodium the martensitic transition appeared to start at about 50 K, which is higher than previously measured values and indicates the sensitivity of the muon as a probe of phase changes.

Muon spin relaxation has been demonstrated to be a suitable technique for investigating phase changes occurring gradually as a function of temperature. As the muon is an interstitial particle, it is strongly affected by its local environment. This enables certain phase transitions to be readily identified using muon spin relaxation, which are difficult to study with other techniques.

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