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Do the measurements of ^{27}Al and ^{7}Li Knight shifts have any analytical role in studies of freshly prepared lithium aluminium alloys?

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Abstract—^{27}Al and ^{7}Li Knight shifts have been measured for a series of freshly prepared Li/Al alloys. The phase diagram implies that three phases should be accessible for the compositions (up to 6% Li) considered and it is shown that, particularly in the ^{27}Al spectra, three Knight-shifted resonances are observable for several compositions. It is suggested that these might correspond to the three phases (α, δ, δ'). The resonance believed to be associated with the δ' phase is sensitive to the lithium content, but changes discontinuously when precipitation of the cubic δ phase (LiAl) occurs. © 1997 Elsevier Science Ltd

The first example of a commercial lithium aluminium alloy (Scleron) was reported in 1925 [1], but its commercial success was short lived. There was a revival of interest in these materials in the 1940s, but the introduction of non-lithium containing alloys such as 7075 in 1943 (Al/6.1Zn/2.9MG/2.0Cu/0.5Fe/0.4Si/0.35Cr/0.3Mn) again diverted attention to alternative systems. The work of Hardy [2] in 1955 reawakened interest which culminated in the development of alloy X-2020 [3] (Al/4.5Cu/1.1Li/0.5Mn/0.2Cd). The new alloy was tested extensively in aircraft but, although many properties were excellent, poor fatigue behaviour led to discontinuation of the programme. Interest in the materials shifted to the U.K. [4], where work concentrated on the Al/Li/Cu/Mg system, which showed the best balance between strength and fracture toughness. An alloy designated 8090 was ultimately registered, followed by 8091 both of which are available commercially.

A problem with the alloys of aluminium and lithium arises when attempts are made to cast them either in sand or in investment moulds: metal–mould reactions cause spoliation of the cast surface. It is also a fact that accurate and rapid measurement of lithium content

is difficult. During work developed in the authors' laboratories to identify the cause of the metal–mould reactions, much use was made of solid-state NMR and in some experiments (^{27}Al, ^{7}Li and ^{6}Li) on material that contained alloy particles, extremely large down-field shifts were seen, characteristic of the metallic phase. These are the well documented Knight shifts [5]. It was then speculated that the Knight shifts of lithium–aluminium alloys may be of analytical value in that the shifts could reflect the phases present and perhaps even the concentration of lithium in the alloy.

The phase diagram [6] for the binary Li/Al system in the 0–6% Li region suggests that three phases should be accessible:

α—Based on pure aluminium with a maximum solubility of Li of up to 14 atomic per cent.

$\alpha + \delta$—An intermediate two phase equilibrium containing the Li solution and δ an AlLi intermetallic compound.

δ'—A metastable ordered phase of composition Al$_3$Li which precipitates within the $\alpha + \delta$ equilibrium.

Of chemical interest is the fact that the δ phase is cubic (NaTl type) [7,8]. There is much in the metallurgical literature on the relationship between the δ

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and δ' phases, including at least one attempt to suggest a mechanism of how δ is formed from δ' [9]. In this paper we report observations on ^{27}Al and ^{7}Li Knight shifts from freshly prepared Li/Al alloys as well as from other alloys containing additions of Mg and of Cu. Despite a reasonable level of interest in Knight shifts in the current literature, no recent application to the study of these alloy systems has been located. Some encouragement may be obtained from an early study of some thallium alloys using ^{205}Tl NMR in which it was shown that the observed chemical shift varied continuously with composition within a phase, but that discontinuities were noted when phase transitions occurred [10].

EXPERIMENTAL

Preparation of the alloys

Aluminium of 99.9% purity was obtained from Alcan Ltd, Kitts Green, Birmingham, U.K.; lithium was obtained from Aldrich. Salamander graphite crucibles (Thomas Sutton Ltd, Birmingham, U.K.) were used to contain the metal components and heating was *via* a Carbolite furnace. The furnace was modified to allow an argon (dried by passage through silica gel and 4 Å molecular sieves) line to be introduced such that the metals could be melted under a blanket of inert gas.

In a typical procedure, the requisite quantity of aluminium was weighted into the graphite crucible which had previously been heated to the normal operating temperature of 750°C and stored in a desiccator. The furnace temperature was set at 750°C and the crucible was introduced and left for 35 min, at which point the argon flow was started. After a further 10 min, a flux of dry LiCl/KCl (1 : 1) was added to the crucible to remove any contaminants which rise to the surface of the molten metal—once effervescence had ceased the flux was carefully removed and the crucible returned to the furnace for 5 min to regain the initial temperature. The crucible was removed and placed under a "hood" to provide a blanket of argon, the lithium, each piece wrapped in pure aluminium foil, was added, piece by piece, to the crucible and held under the surface until reaction had subsided. On completion of the lithium addition, the alloy was poured into a brass mould and allowed to cool to room temperature. Small quantities of magnesium (m.pt 651°C) could be dealt with in a similar manner, but copper (m.pt 1083°C) had to be treated differently. In the latter case, the aluminium, in the presence of the desired quantity of copper, was initially heated to 1100°C and the melt temperature was then dropped to 750°C and the above procedure was followed for the addition of lithium and magnesium.

Analysis of the alloys

Atomic absorption spectroscopy (Perkin–Elmer 373 instrument) was used to determine the secondary metal content of the alloys. Initial digestion was in hydrochloric acid in plastic beakers following which standard procedures for AA analysis were employed.

NMR analysis of the alloys

All spectra were obtained using the "magic" angle spinning (MAS) technique with a Bruker AC300 instrument fitted with a BL7 probe. ^{7}Li spectra were recorded at 116.644 MHz and referenced to aqueous LiCl; ^{27}Al data were obtained at 78.205 MHz and referenced to $[Al(H_2O)]^{3+}$. Considerable difficulty was experienced in getting the samples to spin, possibly because of rotor imbalance and the effects of eddy currents. The problem was solved by reducing the alloys to a powder and sieving and the fraction of < 53 μ was used to pack the zirconium oxide rotors. Under these conditions stable spinning rates of approximately 3500 Hz were obtained for alloys with Li contents of $<3\%$, but when the Li content was greater spinning speeds of 5000 Hz were attainable, although no explanation can be offered for this experimental fact. A consequence of using relatively low spinning rates was that the spectra contained progressions of spinning side bands (SSB). A typical Knight-shifted ^{7}Li resonance of the commercial alloy 8090 is shown in Fig. 1 and Figs 2 and 3 illustrate spectra of alloys prepared in this work. Overlap of spinning side band progression for the resonances at lower field made attempts to estimate $\Gamma_{1/2}$ (full width at half maximum) unreliable, hence no estimates are included. For the broad bands the errors in estimating the maxima are of the order of ± 25 ppm.

RESULTS AND DISCUSSION

The NMR spectra were obtained using the standard "magic" angle spinning technique, which involves coherent motion about an axis inclined at 54.74° to the applied magnetic field. The technique is effective in removing dipolar interactions, but for nuclei with nuclear spin $(I) > 1/2$ in non-cubic environments second order quadrupole effects are not averaged to zero by the experiment. Both ^{27}Al ($I = 5.2, 100\%$) and ^{7}Li ($I = 3/2, 92.5\%$) are quadrupolar nuclei and thus, when the atoms are in a non-cubic environment, broad lines may be observed the maxima of which do not necessarily correspond to the isotropic chemical shifts.

Binary lithium–aluminium alloys

The alloys were prepared as described above; it will be noted that although the materials were not chilled, the cooling to room temperature was a relatively rapid process. Analysis of the alloys were carried out as soon as possible following preparation and no attempt was made to anneal the metals. It will, however, be appreciated that the alloys had to be worked to reduce
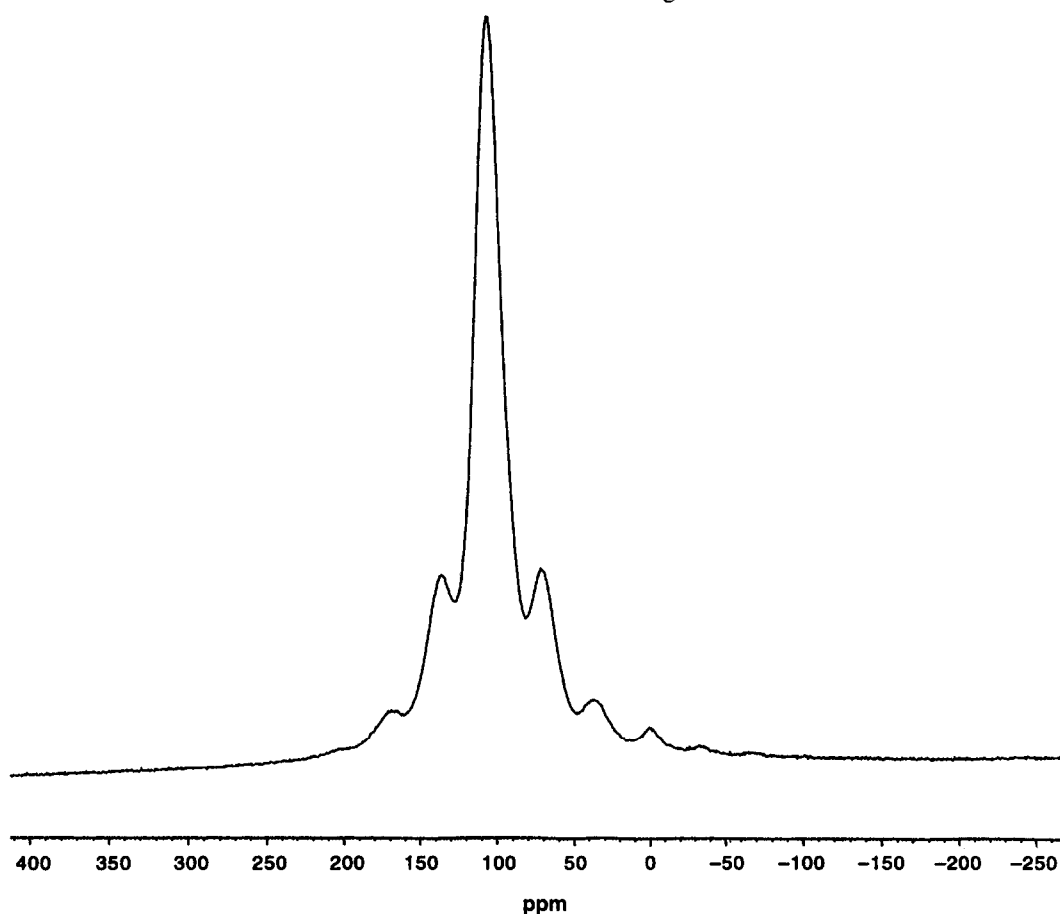
Fig. 1. The ^{7}Li NMR spectrum of the commercial alloy 8090 (Al, Li, Mg, Cu).

them to powders, hence the reported NMR data relate to the worked powders. It must therefore be allowed that, since metals are subject to skin depth problems, the working may alter the surface properties.

Table 1 details the observed NMR data and includes the lithium content as determined by atomic absorbtion spectroscopy. Figures 2 and 3 show the spectra obtained for the 6.13 and 5.03% lithium alloys. It will be noted that a particularly unsatisfactory spectrum was obtained (^{27}Al) for the 3.06% Li/Al alloy, within which the overlap of three complex spinning side band sequences could be discerned; for that reason it is not sensible to report numbers in the table for this composition (NB higher spin rates were possible when the Li content was greater than 3%). Alloys with lithium contents of >3–4% show three distinct Knight-shifted resonances in the ^{27}Al spectra. The Li/Al phase diagram, which is taken to be well established and to provide a useful guide to interpretation, suggests that the α, δ and δ' phases may indeed be accessible within the range of Li percentages used. Given that δ is a cubic 1 : 1 intermetallic phase a sharp resonance for both ^{27}Al and ^{7}Li with no second-order quadrupolar broadening may be anticipated; the resonance observed for ^{27}Al between 166 and 171 ppm is

ascribed to this phase. Although these numbers are rather small for ^{27}Al Knight-shifts, they cannot be credibly assigned to other aluminium containing phases; also the relatively narrow line width ($\Gamma_{1/2} = 120$ Hz) is consistent with a cubic environment for the aluminium. Andrew et al. [11] report an accurate Knight-shift for pure aluminium of 1650 ppm vs $[Al(H_2O)_6]^{3+}$, thus the resonance close to 1640 ppm is the most likely candidate for the α-phase, which is based on pure aluminium with up to 14 atom percent Li in solution. It is, however, the remaining resonance which appears most sensitive to lithium content, if the δ'-phase is indeed stoichiometric, e.g. Al$_3$Li, this observation is surprising. However, it has been suggested [9] that the phase is non-stoichiometric and has sufficient vacancies to absorb Li, in which case the asymmetry parameter would change and this would lead to a change in the observed peak maximum given that the "shifts" observed are not the isotropic shifts. Hence, given that δ is only observed when the lithium percentage is >3, it may be argued that these data provide support for the hypothesis that lithium is absorbed by the δ'-phase until the point at which some δ material can crystallize. When the lithium percentage is low (<1%), only a single line cor-

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Table 1. Knight-shifted resonances from freshly prepared binary lithium–aluminium alloys

%Lithium (AA)[a]	[27]Al resonances[b]	[7]Li resonances[c]
6.9	1643 (sharp)	103 (asymm)
	1286 (broad)	
	166 ($\Gamma_{1/2} = 120$ Hz) (sharp)	−1.88
6.13	1640 (sharp)	104 (asymm)
	1410 (broad)	
	171 ($\Gamma_{1/2} = 120$ Hz) (sharp)	−1.7
5.03	1660 (sharp)	105
	1408 (broad)	91
	168 ($\Gamma_{1/2} = 120$ Hz) (sharp)	−1.17
4.25	∼1670 (broad)	∼101
	∼1409	
	150–200 (SSB overlap)	0.55
3.06	Severe SSB overlap from 3 resonances	103 (assymm)
		1.07
0.95	1644	102
0.49	1625	103

[a] Atomic absorption.
[b] ppm *vs* [Al(H$_2$O)$_6$]$^{3+}$
[c] ppm *vs* aqueous LiCl.

Table 2. Knight-shifted resonances for freshly prepared ternary lithium–magnesium–aluminium alloys

%Li (AA)[a]	%Mg (AA)[a]	[27]Al resonances[b]	[7]Li resonances[c]
0.197	0.129	1693	106
		1451	
0.69	0.233	1688	104
		1440	
2.10	0.123	1630	103
		1328	
2.18	0.613	1614	106
		1347	4.7 (very weak)
2.94	0.235	1696	101
		1326	92
			2.14
6.0	0.50	1351	102 (assymm)
		192	−3.0 (sharp)

[a] Atomic absorption.
[b] ppm *vs* [Al(H$_2$O)$_6$]$^{3+}$.
[c] ppm *vs* aqueous LiCl.

responding to the α-phase is observed. The [7]Li spectra were also examined. An asymmetric resonance at 101–103 ppm *vs* aqueous LiCl is seen when the lithium content is >3%; for low lithium concentrations the line is symmetrical, thus there is supporting evidence from the [7]Li spectra for the presence of two phases (α+δ'), which give normally unresolved Knight-shifted resonances in the 100 ppm region. However, when the percentage lithium = 5.03%, resolution of the lithium line is achieved. In addition a resonance at approximately −1.75 ppm is seen when the Li content is >3%. It must be considered that this resonance arises from a surface layer of Li$_2$O and/or Li(OH) but it is possible that it relates to the AlLi δ-phase, which gives the relatively small [27]Al Knight shift referred to above.

Ternary lithium–aluminium–magnesium alloys

Although attempts were made to keep the %Li constant, and vary the magnesium content, the AA analytical data (Table 2) show that the objective was not achieved. This is, in fact, fortuitous since the [27]Al

NMR data (Table 2) show two phases in the lithium range 0.2–3.0%; one is characterized by a relatively invariant resonance (1656 ± 40 ppm), the other varying monotonically with the percentage of lithium present. Following the above discussion the relatively invariant resonance is assigned to the α-phase and the resonance in the range 1450–1325 ppm to the δ'-phase. Apparently the presence of the magnesium has promoted the formation of the δ'-phase in contrast to what is observed for the low lithium binary systems. Superficially it would appear that magnesium has little influence on the observed chemical shifts. In one case (Table 2) when the Li content was 6.0%, evidence of the δ-phase was again noted (although in this case no α-phase is discernable). It is interesting that a discontinuity of the chemical shift to the δ'-phase occurs at the point of precipitation of the δ-phase, not unlike the earlier report on Tl alloys [10].

Quaternary lithium–aluminium–magnesium–copper alloys

Only alloys with lithium contents in the range 0.7–2.5% were prepared (see Table 3), thus, given the above discussion, it is not surprising that no evidence of the δ-phase was seen. The α-phase seems to be suppressed, particularly when the alloying elements are present at the order of 1% or more, hence, this series, which most closely approximates the commercial alloys, is the most homogeneous in composition as freshly prepared.

Conclusions

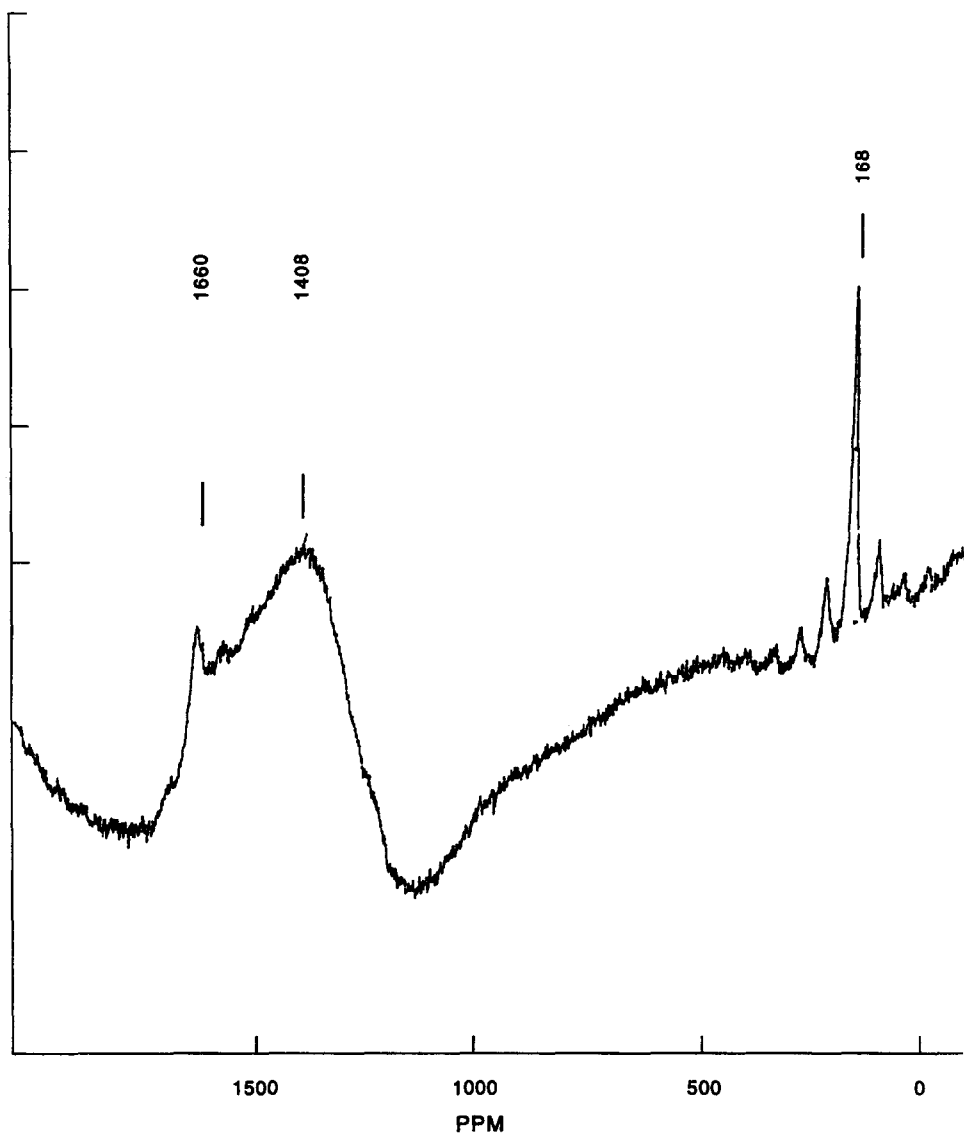The Knight-shifts measured for the aluminium and, to a lesser extent, the lithium NMR resonances of a

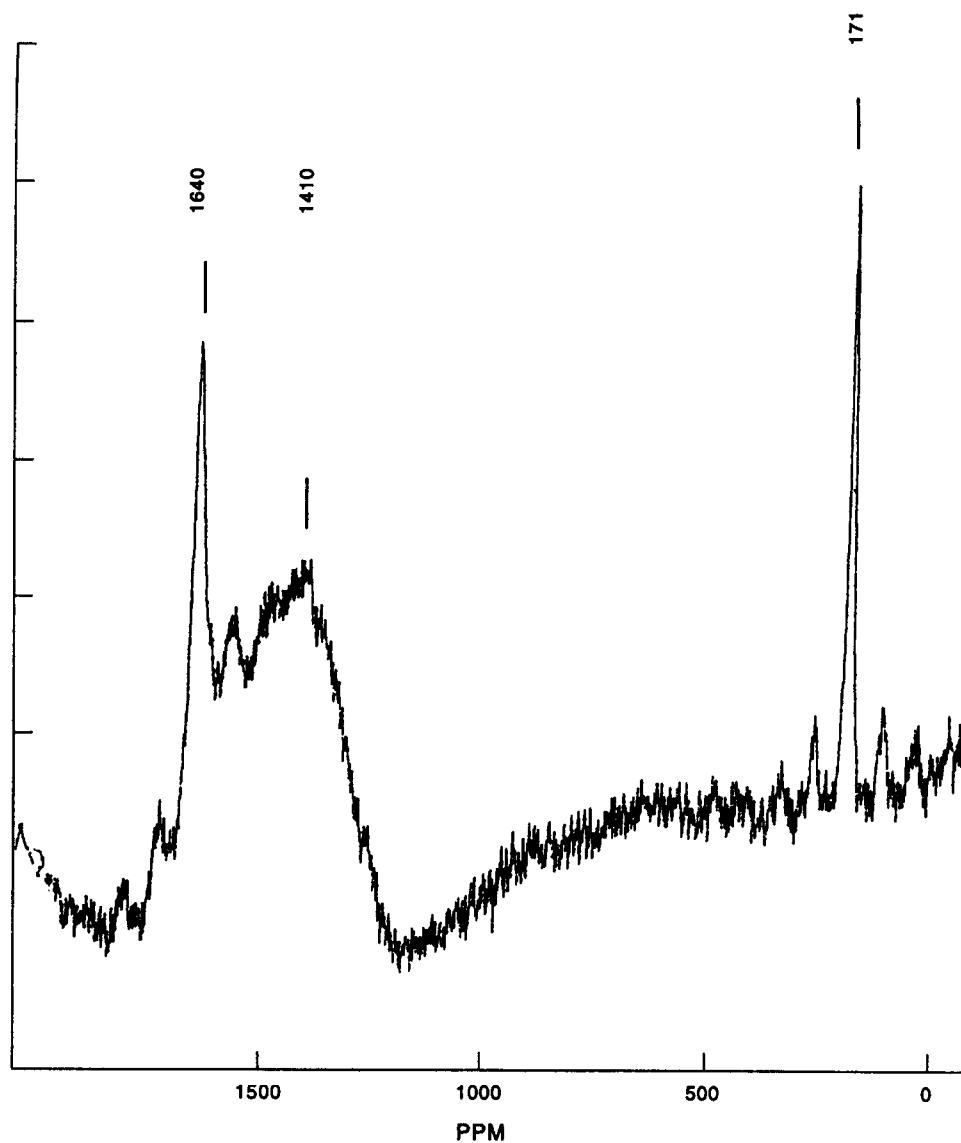Fig. 2. The ^{27}Al NMR spectrum of a binary Li/Al alloy (5.03% Li).

Fig. 3. The ²⁷Al NMR spectrum of a binary Li/Al alloy (6.13% Li).

Table 3. Knight-shifted resonances from freshly prepared quaternary lithium–magnesium–copper–aluminium alloys

%Li (AA)[a]	%Mg (AA)[a]	%Cu (AA)[a]	²⁷Al resonances	⁷Li resonances
0.71	0.04	0.31	1691 1429	103
1.49	0.06	0.10	1622 (weak) 1340	103
2.50	1.00	1.60	1380	103

[a] Atomic absorption.
[b] ppm *vs* [Al(H₂O)₆]³⁺.
[c] ppm *vs* aqueous LiCl.

series of lithium/aluminium alloys qualitatively reflect the fact that several phases are present in a given alloy composition. Use has been made of the established phase diagram, together with structural information on the various phases in the literature, to suggest tentative assignments of Knight-shifts to specific phases. On this basis there is evidence that the δ'-phase can absorb lithium until precipitation of the 1:1 cubic intermetallic compound LiAl commences; prior to the precipitation of the δ-phase, the "chemical shift" of the δ'-phase varies monotonically with the lithium content of the alloy.

If spin-lattice relaxation times (T_1) were measured, it should be possible to obtain quantitative data, thus Knight-shift measurements could provide a possible means of investigating phase compositions.

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