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NMR study of Li in Al-Li-Cu icosahedral alloys

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Nuclear magnetic resonance (NMR) results are presented for lithium in several powder samples with a composition near Al_6Li_3Cu which suggest a strong relationship between the cubic *R* phase and the icosahedral phase. All NMR spectra show a broad component which arises from a site in *R*-phase samples as well as what appears to be a similar site in the icosahedral phase. The pure *R* phase and samples with an appreciable amount of *R*-phase material exhibit a second very narrow peak attributable to Li atoms undergoing rapid motion at a different and perhaps interstitial site.

The recent observation that solids can crystallize into a structure which exhibits a diffraction pattern with icosahedral point symmetry has led to many investigations into such structures.[1,2] Models for the icosahedral phase have included quasiperiodic structures, glasses with icosahedral orientational order, and twinned large-unit-cell crystals. In keeping with current usage, we will refer to these materials as quasicrystals.

Initial experimental investigations centered on the Al-Mn alloys and have yet to reach conclusive results regarding the detailed crystal structure. This is particularly true for the nuclear magnetic resonance (NMR) studies[3–7] due to the large distributions in the Knight shift and quadrupole interactions, the small grain size of the material, and the possibility that some of the Mn sites may not be observable by NMR due to Mn magnetic moments. We have undertaken a NMR study of the ^7Li and ^6Li resonances in a different system, an alloy of Al, Li, and Cu,[2,8] where these difficulties are not present.

We report here that the Li resonance from the quasicrystal materials appears to be a single symmetric line, even in powder samples, characteristic of a single Li site with a relatively high symmetry. This is in direct contrast to the Mn signal in the Al-Mn quasicrystal alloys where a distribution in sites is overwhelmingly evident. Furthermore, this single site is indistinguishable from one of two sites observed in the cubic *R* phase (or Frank-Kasper phase) with a similar composition.

EXPERIMENT

The majority of the NMR measurements were obtained at room temperature using a magnetic field of 35.3 kG. In all cases they are referenced to the Li signal from a saturated aqueous solution of Li_2CO_3. Free-induction decays were Fourier-transformed to obtain NMR spectra. Hahn and solid echoes[9–12] were used to characterize the spin-spin relaxation time T_2 and inversion-recovery sequences were used to measure the spin-lattice relaxation time T_1. To help understand the nature of the observations, additional measurements were made at temperatures down to 77 K and for both ^7Li and ^6Li in a magnetic field of 85 kG.

Seven samples with starting compositions near Al_6Li_3Cu were prepared (see Table I) using techniques described elsewhere.[2,5] Three of the samples were taken from the ingot after melting the elements and the other four were from melt-spun ribbons. X-ray analysis showed that some of the samples were a mixture in different degrees of the crystalline *R* phase, the icosahedral phase, and aluminum. For comparison, a 50-50 mixture of Al and Li and a pure Li-metal sample were also prepared and measured. The Li and Al-Li results are in agreement with previously published data.[9,10,13,14] All samples were a collection of randomly oriented particles.

RESULTS AND DISCUSSION

The room-temperature NMR spectra obtained near 58.5 MHz for all of the samples are shown in Fig. 1. The NMR spectra all have a broad symmetric line and some have an additional very narrow line. The relative intensity of the narrow line, ranging from a maximum of roughly 18% of the total intensity in sample I to essentially 0% in samples IV–VI—the samples with no measurable (less than about 5%) *R*-phase component—is clearly very sample dependent, even for the two samples which are nominally pure *R* phase. The narrow line shows a negligible shift relative to the aqueous standard as is the case for Al-Li. In contrast, the shift for Li metal is roughly 15.5 kHz towards higher frequency. Cooling the sample

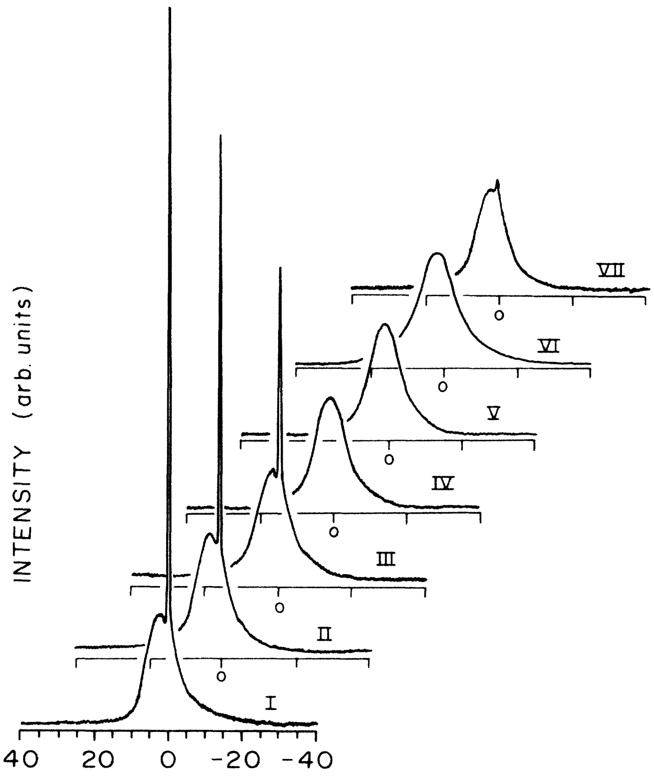

FIG. 1. Room-temperature NMR spectra obtained near 58.5 MHz for the Al-Li-Cu samples. The height of the broad peak has been scaled such that the intensity is the same for all spectra.

shows conclusively that the narrow component is motionally narrowed at room temperature as is observed for both Li metal and Al-Li.[10,13,14] The NMR line begins to broaden around 130 K, the same temperature observed for Al-Li but much lower than the 290 K observed for Li metal. The room-temperature spin-lattice relaxation time T_1 for the narrow component is roughly 0.5 sec. We conclude that the narrow component is the result of non-quasicrystal phases present in the sample, most likely the *R* phase itself, and is of interest only in contrast to the absence of this peak in all samples which are entirely quasicrystalline. Indeed, considering the spectra to be a combination of the pure *R* and pure icosahedral phases yields, with the exception of the Cu-rich sample VII, a consistent ratio of narrow to broad peak intensities.

The broad line shows a small but significant shift towards higher frequencies. The shift, expressed as a fraction of the operating frequency, is independent of magnetic field, indicating that it is either a chemical shift, a Knight shift, or a combination of the two. A Knight shift will show the characteristic Korringa temperature (T) dependence, $T_1T=\text{const}$, independent of operating frequency. Indeed, that is what is observed between 77 K and room temperature with $T_1T=1100$ sec K and is illustrated in Fig. 2. One can estimate the size of the constant to be 2000 sec K based on the magnitude of the measured shift using parameters appropriate for a noninteracting-electron model. A discrepancy between calculated and measured values is to be expected[10] and in this case may be exacerbated by the small size of the shift and the uncertainty as to the correct zero of the shift. We conclude that the shift we observe is in large part the

TABLE I. Sample characteristics and NMR results for the broad component obtained at 58.5 MHz and room temperature. The relative amounts of icosahedral phase (*I*), cubic *R* phase (*R*), and metallic aluminum (Al) are estimates based on powder x-ray diffraction intensities. A negative NMR shift corresponds to higher frequencies for a constant magnetic field.

Sample	Relative concentrations Al	Li	Cu	Relative intensity of broad to narrow line for the *R* phase[a]	NMR shift (ppm)	Width (FWHM)[b] (kHz)	T_1 (sec)	Comments
I	55	34	11	5:1	−27±3	9.8±0.5	2.6±0.3	ingot, pure *R* phase, trace of Al
II	57	33	10	4:1	−32	9.6	3.1	ingot, approximately $\frac{1}{3}$ *R* phase, $\frac{1}{3}$ *I* phase; $\frac{1}{3}$ Al
III	55	34	11	4:1	−29	10.0	2.9	ribbon, ~75% *I* phase remainder *R* phase
IV	57	33	10		−25	10.0	3.3	ribbon, pure *I* phase
V	57	33	10		−25	10.2	2.7	annealed ribbon, *I* phase with trace of Al
VI	59.2	31.2	9.6		−22	9.8	4.0	ribbon, I phase with small amount of Al (~10%)
VII	57	30	13	150:1	−29	10.0	2.7	ingot, *R* phase with small amount of Al (~10%)

[a] Contribution of broad-line intensity due to *R* phases estimated from x-ray analysis. See comments.

[b] FWHM denotes full width at half maximum.

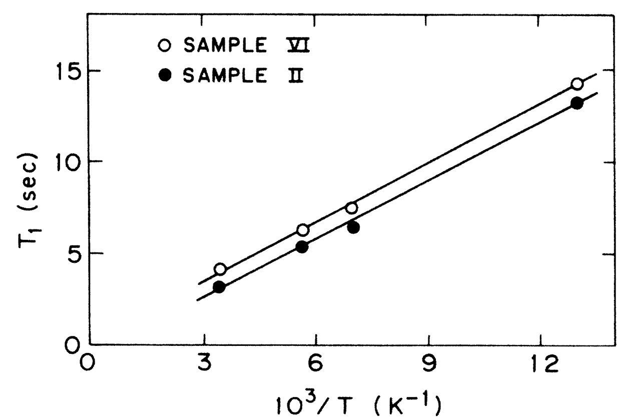

FIG. 2. The spin-lattice relaxation time T_1 vs inverse temperature $1/T$, showing the Korringa straight-line behavior.

Knight shift due to conduction electrons. Measured values for the shift and room-temperature spin-lattice relaxation T_1 are included in Table I.

That the Knight shift is small indicates that the density of states at the Fermi surface as seen by the Li nucleus is small compared to Li metal, but not as small as is the case for the Al-Li mixture. In a linear combination of atomic orbitals framework one would say that the contribution to the conduction band at the Fermi level from Li orbits is small.

The sample dependence of the Knight shift is larger than experimental error, as is clearly seen in the high-field data shown in Fig. 3. As yet, we have found no correlation between the differences in the shift and the sample characteristics, except perhaps the amount of Al metal present. One possibility is that point defects such as Li vacancies and Li substitutions on Al or Cu sites, which are necessary to explain the observed electronic structure in Al-Li, strongly affect the shift, as has been observed for the Al-Li system.[15,16] The role of such defects in quasicrystal formation should be investigated further.

To determine the nature of the interaction(s) which give rise to the linewidths (see Table I) of the broad component, Hahn and solid echoes were used. In all cases the decay of the echo amplitude was exponential over the first two time constants with a time constant corresponding to the observed linewidth. The ^{7}Li linewidth at higher fields was, within error, the same as that at lower fields and the same as seen in the Al-Li mixture and the Li sample at 77 K, where the Li motion is frozen out. In addition, despite the high signal-to-noise ratio, the satellites characteristic of a quadrupole powder pattern are not evident in the line shape. In contrast, the satellites for a powder of Li_2CO_3, which has a dipolar broadening of 8.8 kHz, were easily observable roughly 35–40 kHz on either side of the central line. All of these factors mentioned above suggest that the linewidth is not due to an inhomogeneous distribution of NMR frequencies, but is simply due to the nuclear dipole-dipole broadening. The shift anisotropy and quadrupole interactions appear negligible in comparison.

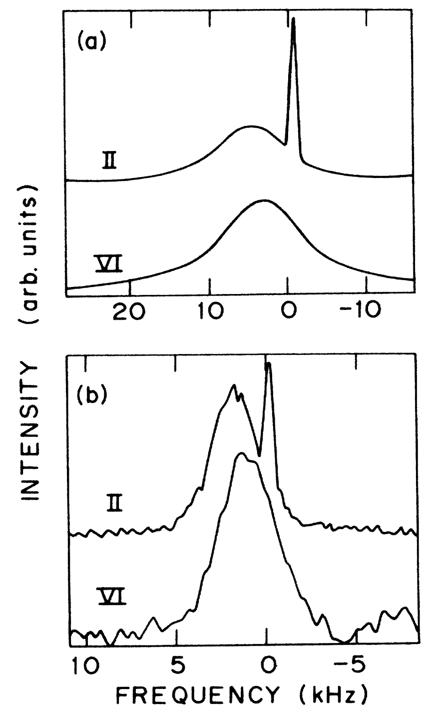

FIG. 3. Room-temperature (a) ^{7}Li and (b) ^{6}Li NMR spectra obtained near 139.8 and 52.9 MHz, respectively, for two of the quasicrystal samples.

The higher-field data shown in Fig. 3 for two of the samples confirm these conclusions. Data were obtained for natural abundance ^{7}Li and ^{6}Li. To a good approximation, both isotopes experience the same local environment; however, their NMR parameters are very different.

If the linewidth is dipolar, ignoring interactions with neighboring ^{6}Li nuclei due to its low natural abundance, the ratio of the linewidths for ^{6}Li and ^{7}Li should be between 2.64 and 3.96, depending on whether the neighboring nuclei are predominately Al and/or Cu or predominately ^{7}Li, respectively.[9] We observe a ratio of 2.9 ± 0.2 for the two samples.

The ratios of the intensities of the broad to narrow components for sample II are equal (8:1) within 20% for the two isotopes. This sets an upper limit on the size of the quadrupole field that may be present. Since ^{6}Li has a spin, $I=1$, the -1 to 0 and the 0 to $+1$ transitions are affected in opposite directions to first order in the quadrupole field. One can easily see that the quadrupole field splitting is negligible for the ^{6}Li data. However, ^{7}Li has a spin, $I=\frac{3}{2}$, and a quadrupole moment 43 times larger than that of ^{6}Li. The $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ transitions may be affected strongly to first order with the $+\frac{1}{2}$ to $-\frac{1}{2}$ transitions broadened negligibly in second order. This would diminish the observed intensity of the broad component by roughly a factor of 2 compared to the narrow component. The equality of the ratios of the intensities of the broad to narrow components shows that the $\frac{3}{2}$ to $\frac{1}{2}$ transitions are not broadened outside the 10-kHz linewidth of the signal. Thus we conclude that the quadrupole field is no larger than roughly one-tenth the size observed for Li_2CO_3.

STRUCTURAL CONSIDERATIONS

The single symmetric broad NMR line observed in all samples with a field-independent width, and spin-spin relaxation following a single-exponential behavior, comprise evidence for a single type of Li site and that the site is relatively symmetric. This is surprising since in some cases we are clearly looking at a sample containing two different lithium-containing phases. We can only conclude that at least locally the Li site in the quasicrystal is virtually identical to one of the sites in the R-phase material.

As a word of caution we point out that one can observe a single symmetric NMR line in cases where there is structurally more than one type of site. The success of NMR as a probe of nuclear environments is due, in part, to the fact that such situations are rare. We also note that symmetric NMR patterns can be seen from asymmetric environments, especially in cases where (local) motion is present. Motion can be detected by cooling the sample and noting changes in the NMR parameters. We have seen no changes in the broad component of the spectrum that can be associated with motion down to 77 K.

Recent x-ray- and neutron-scattering measurements[17–20] support our interpretation. The local structure, up to 20 Å, of both the icosahedral and R phase appears to be very similar, and they share the same local rhombohedral building block,[18,19] though the Li environment is not quite the same in these two phases. In the icosahedral phase Li atoms occupy essentially one type of site inside the rhombohedral unit cell[17,19,20] with nearest-neighbor Al and Cu atoms at around 3 Å.[18–20] The R phase, on the other hand, is made of a bcc packing of locally icosahedral clusters,[19,20] and Li atoms occupy two different sites. One is inside the icosahedral clusters and is very similar to the Li site in the icosahedral phase (D and E sites, Ref. 19). This site is most likely the one which gives rise to the broad NMR lines. The second site is in between the icosahedral clusters (H site, Ref. 19). This site could be the origin of the motionally narrowed NMR line. Interestingly, the relative amounts of the two components in Ref. 19 are in the ratio of approximately 3.5:1, in reasonable agreement with the NMR experiment.

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