

β -NMR Study of the Electric Field Gradient in the Metallic Intercalation Compound LiC_6

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In the layered compound LiC_6 polarized β -active ^8Li probe nuclei were produced by capture of polarized thermal neutrons. Nuclear magnetic resonance spectra of ^8Li were recorded via the β -radiation asymmetry. The ^8Li quadrupole coupling constant e^2qQ/h , measured in the temperature range $T = 5 \dots 500$ K, decreases with increasing T from 45.2(8) to 22.8(4) kHz. Anomalies in the overall temperature dependence are discussed in terms of phase transitions proposed for LiC_6 .

1. Introduction

A characteristic feature of graphite intercalation compounds (GICs) is the variety of ordered structures and phase transitions observed. A GIC of stage n is formed by a periodic arrangement of one layer of intercalant followed by n layers of graphite. Both intercalant in-plane order and layer sequence are known to undergo various phase transitions for many intercalant species [1].

LiC_6 is a stage-1 intercalation compound with a particularly simple lattice structure at room temperature [2], as shown in Figure 1. In contrast to

graphite the carbon layers are stacked in direct registry with respect to each other. The lithium atoms, being sandwiched between two carbon layers such that one-third of the C hexagons have Li atoms directly above and below, form a 2D hexagonal superlattice ($\sqrt{3} \times \sqrt{3} R$ 30° structure: the Li-superlattice vectors are measured in units of the graphite lattice, their direction is obtained by 30° rotation of the graphite lattice vectors). This phase is stable [3, 4] from the Li-superlattice melting temperature $T = 715$ K down to at least $T \cong 230$ K. The question whether this staging sequence persists to lower temperatures is subject to experimental controversy [3–5, 12, 18] and evokes theoretical interest [6]. The present investigation of the electric field gradient (EFG) at the Li-site contributes to this discussion. It is well known that the EFG is highly sensitive to changes of the charge distribution surrounding the probe nucleus. Thus a study of the EFG in a GIC with metallic properties ($\sigma_{\text{in-plane}} = 2.4 \cdot 10^5 \Omega^{-1} \text{cm}^{-1}$ [7]) may provide information about the distribution of conduction electrons. In earlier NMR work on stable ^7Li in powder LiC_6 [8, 9] the EFG was found to change considerably with temperature. By using oriented samples the accuracy could be improved, but data were taken only at the two temperature values 290 K and 4.2 K [10]. In the present study on β -active ^8Li in an oriented sample the EFG was measured in the range $T = 5 \dots 500$ K. Improved accuracy was achieved by observing multiple quantum transitions. The β -NMR method used here turned out to be advantageous for measuring the EFG in this metallic

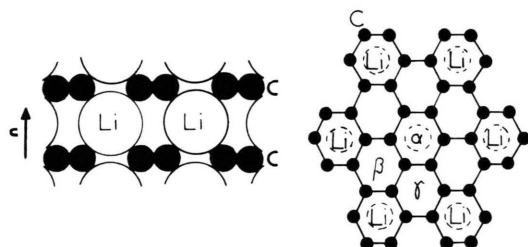


Fig. 1. Structure of LiC_6 . Left side: Cut along c -axis; Right side: Cut along a graphite plane. At room temperature Li occupies only α -sites.

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sample. The polarization of the probe nuclei, which is monitored via their β -radiation asymmetry, stems from the capture of polarized neutrons and is thus independent of any Boltzmann factor. Therefore it is possible to measure the EFG at low magnetic fields without loss of sensitivity. The corresponding frequencies of the external radio frequency (rf) field are sufficiently low to assure good rf-penetration even in the metallic sample used here.

2. Experimental

The experiment was performed using the in-beam β -NMR spectrometer S6 at the high-flux reactor of the Institut Laue-Langevin, Grenoble. Polarized β -active ^8Li ($T_{1/2} = 0.8$ s) probe nuclei were produced in isotope enriched $^7\text{LiC}_6$ by capture of polarized thermal neutrons. The ^8Li polarization was measured via the asymmetry of the β -radiation distribution with respect to an external magnetic field B (for details we refer to [11]). The samples, composed of several cylindrical slabs of 40 mm diameter and about 1 mm thickness, were prepared by H. Zabel. The material $^7\text{LiC}_6$ was obtained by immersing highly oriented pyrolytic graphite (HOPG) and pyrolytic graphite (PG) in molten ^7Li [12]. The HOPG and PG samples had about 3° and 10° mosaic spread, respectively. Control of stage fidelity by elastic neutron scattering gave an upper limit for the stage-2 admixture of about 3%.

3. Physical Background

In LiC_6 the EFG at a ^8Li site is produced by the almost completely ionized Li atoms and the Li valence electrons which are transferred into the nearly empty π -conduction band of pristine graphite [13]. Additionally the valence electrons of the carbon host lattice have to be taken into account.

The temperature dependence of the EFG in metals is often found to obey approximately the empirical relation [14]

$$eq(T) = eq(0)(1 - b T^{3/2}). \quad (1)$$

So far no theoretical model reproducing the analytical form of (1) has been reported. At present thermal lattice vibrations are regarded as being

mainly responsible for the temperature dependence of the EFG in metals [15]. Thermal repopulation effects of Fermi surface electrons and/or phonons smearing out the electron-ion potential thus perturbing the electronic part of the EFG may result in the temperature dependence (1) for an intermediate temperature range (for a review see [15]). As a matter of fact simple variations of lattice constants with temperature are not able to explain the observed strong temperature dependences in most of the cases.

4. Multiple Quantum Spectra

In [16] the multiple quantum NMR technique was shown to possess several advantages when measuring quadrupole coupling constants which are of the same order of magnitude as the dipolar line width. The method consists of equalizing the population of nonadjacent nuclear energy levels by simultaneous absorption of two or more photons. All possible multiple quantum transitions of a nucleus $I = 2$ (^8Li) in a magnetic field B along the crystallographic c -axis and an EFG with rotational symmetry about c are shown in Figure 2.

Starting from a purely dipolar nuclear polarization (which is the case for the ^8Li probe after polarized neutron capture) the saturation of a single quantum transition will reduce the polarization by only 5%. On the other hand, two, three and four quanta transitions will have an effect of 20, 50 and 100% respectively; thus an appreciable enhancement of sensitivity is obtained.

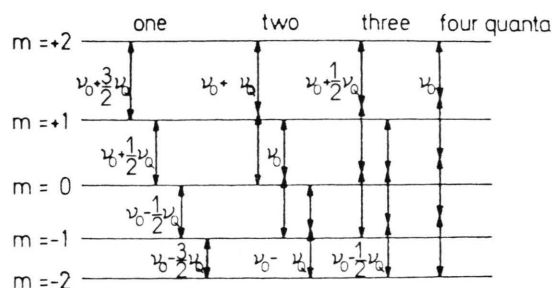


Fig. 2. All possible multiple quantum transitions between the quadrupole shifted nuclear Zeeman levels of ^8Li ($I = 2$). ν_0 : Larmor frequency; ν_q : Quadrupole frequency.

5. Results and Discussion

Figure 3 shows the ^8Li quadrupole resonance spectrum for LiC_6 at $T = 230$ K. In Fig. 4 we plotted the temperature dependence of the quadrupole frequency $\nu_q = e^2qQ/4h$. ν_q decreases strongly from 11.3(2) kHz at $T = 5$ K to 5.7(1) kHz at $T = 500$ K. We also show NMR data on ^7Li [9, 10] scaled with the ratio of the ^8Li and ^7Li quadrupole moments.

The overall temperature dependence follows approximately a $T^{3/2}$ law (note that the temperature scale of Fig. 4 is linear in $T^{3/2}$). However a fit with (1), where the exponent of T was allowed to vary, yields an exponent of 1.44(12). The value for b ($6 \cdot 10^{-5} \text{ K}^{-1.44}$) is a reasonable one, typical values for metals varying between $1 \dots 8 \cdot 10^{-5} \text{ K}^{-3/2}$ [14].

A more detailed inspection of Fig. 4, however, shows a step of the EFG at $T \approx 230$ K. At approximately the same temperature several anomalies were found in different investigations: the spin-lattice relaxation rate of ^8Li shows a discontinuity at $T \approx 230$ K [17]; the electrical conductivity exhibits a weak anomaly just below 200 K [12]; investigation of the specific heat [5] revealed an exothermal effect in the range 170 ... 190 K followed by an endothermal effect in the range 190 ... 210 K. The electron diffraction spot pattern changes around $T \approx 220$ K [18].

The origin of the observed anomalies is still under discussion. Kambe *et al.* [18] interpreted their data in terms of a phase transition of the intercalant stacking sequence. At room temperature the Li ions are known to occupy only α -sites ($\alpha\alpha$ -stacking, see Figure 1). Following [18], $\alpha\beta\gamma$ stacking should occur below $T \approx 220$ K. Such a phase transition would, of course, influence the EFG. If we assume that the valence electron distribution is not altered by the rearrangement of the Li ions, the difference of the EFGs of the two phases is just given by the difference of the Li contributions in the lattice sums. We calculated this value by the plane-wise lattice summation method of de Wette [19]. Inserting the ^8Li quadrupole moment ($Q(^8\text{Li}) = 0.032 \cdot 10^{-24} \text{ cm}^2$ [17]) and the Sternheimer factor of the free Li ion ($1 - \gamma_\infty = 0.744$) we obtain a too high value of

$$\Delta\nu_q = \nu_q(\alpha\beta\gamma) - \nu_q(\alpha\alpha) = 4.8 \text{ kHz}.$$

This discrepancy, however, does not rule out definitively the stacking transition at $T \approx 230$ K because

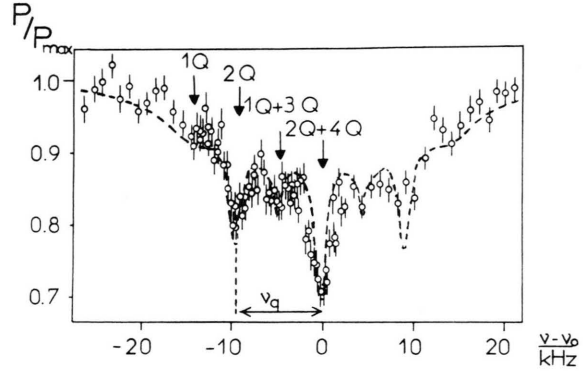


Fig. 3. ^8Li quadrupole resonance spectrum in LiC_6 at $T = 230$ K, static magnetic induction $B = 37$ mT (Larmor frequency $\nu_0 = 0.23$ MHz); broken line: lineshape for $\nu_q = 9.3$ kHz, calculated by use of a computer program described in [16]. The lineshape is a weighted superposition for the two rf fields 1 mT and 0.1 mT (adjusted to yield a good agreement with our data), thus taking into account the skin effect.

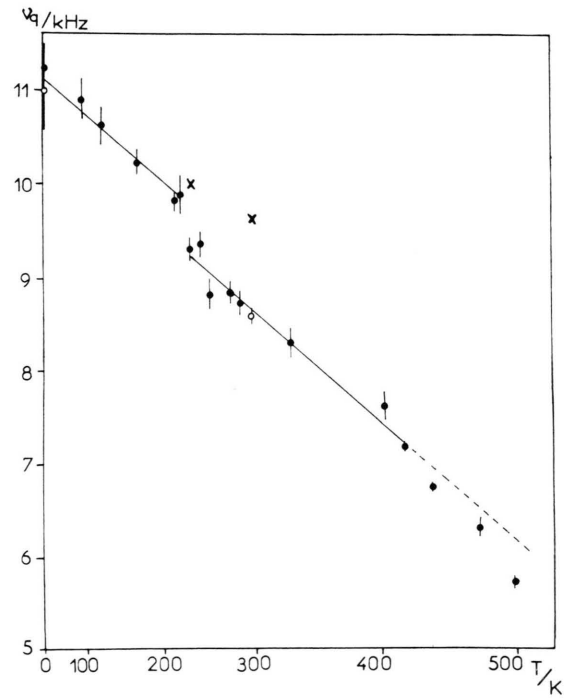


Fig. 4. Temperature dependence of the quadrupole frequency $\nu_q = e^2qQ/4h$.

● this work: $^8\text{LiC}_6$ } oriented samples;
○ Ref. [10a]: $^7\text{LiC}_6$ }
× Ref. [9]: $^7\text{LiC}_6$ powder sample; full lines: guides to the eye.

small changes in the π -electron distribution near the Li site might change the electronic contribution to the EFG considerably. Unfortunately, the valence electron distribution has been calculated only for the $\alpha\alpha$ -phase [13]. On the other hand a search for the stacking transition by elastic neutron scattering [3, 4] failed. Furthermore, according to a recent theoretical study [6], the $\alpha\alpha$ phase should be stable down to lowest temperatures. In conclusion we note that the step of the EFG at $T \approx 230$ K as well as the anomalies mentioned above are presently not understood.

We calculated the total EFG by the method of de Wette [19] under simple assumptions for the valence charge distribution. The uniform background model (Li ions immersed in a homogeneous negative charge distribution) gives $\nu_q(^8\text{Li}, 300\text{ K}) = 3.7$ kHz which is smaller than the measured EFG. The value of the point charge model (the Li ions are surrounded by point charges of $-e/6$ at the carbon sites), however, is much too large: $\nu_q(^8\text{Li}, 300\text{ K}) = 19.4$ kHz. A modified point charge model was used in [9] to explain changes of the EFG with the pressure. All these simple models, however, fail to explain the strong variation with temperature. This is not surprising because they neglect the lattice dynamics and represent quite poorly the valence charge distribution computed in [13]. Notably the latter shows an appreciable amount of π -electron density near a Li site. We estimate this local effect to play an important role for the EFG.

The quadrupole coupling constants of ^7Li in LiC_6 [HOPG] measured by Roth *et al.* [10] agree well

with our data (in Fig. 4 the different quadrupole moments of ^7Li and ^8Li have been taken into account). The discrepancy with the powder values [9] (Fig. 4) might be explained by an orientation of the powder crystallites induced by an external magnetic field B [10b]. An alignment of $c//B$ would enhance the quadrupole splitting over the expected powder value.

Finally, it should be noted that for Li_xC_6 compounds the (T, x) phase diagram [7], at a certain value $x < 1$, shows a first-order transition from a mixed stage at low T to a pure stage – 1 compound at high T by reduction of the Li in-plane density. However, for all concentrations x investigated in [7] the transition temperature lies above 400 K. Since our sample has a stage-2 content of $\lesssim 3\%$ at room temperature (see Chapt. 2) it can be concluded that as much as several per cent of Li vacancies occur in the high temperature phase. This should influence the EFG and by a change of the lattice dynamics also its temperature dependence. Nevertheless, no drastic effect on the EFG around $T \approx 400$ K is observed. Just the slight change in the slope of the EFG vs. $T^{3/2}$ above 400 K might be explained in the framework of this phase transition.

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