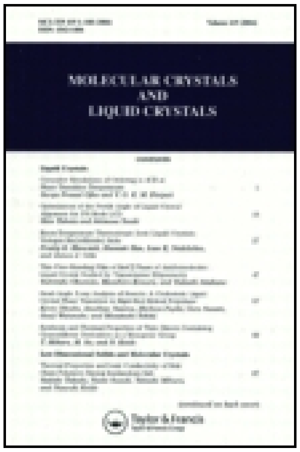

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Conduction-Electron Induced Spin-Lattice Relaxation of ^{8}Li in the High-Pressure Phase LiC_2

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Version of record first published: 04 Oct 2006

To cite this article: A. Schirmer, P. Heitjans & V. A. Nalimova (1998): Conduction-Electron Induced Spin-Lattice Relaxation of ^{8}Li in the High-Pressure Phase LiC_2 , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 291-296

To link to this article: http://dx.doi.org/10.1080/10587259808045351

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 291–296
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Conduction-Electron Induced Spin-Lattice Relaxation of ^{8}Li in the High-Pressure Phase LiC$_2$

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In the superdense stage-1 compound of the LiC$_x$ *system the* spin-lattice relaxation rate T_1^{-1} of ^{8}Li ($T_{1/2} = 0.8$ s) was measured with the β-NMR method. The T_1^{-1} measurements were done in the ampoules of the high-pressure intercalation synthesis and covered the temperature range between 4.2 K and 320 K and external $\vec{B}$ fields between 8.2 mT and 1.7 T for the orientations $\vec{B}||\vec{c}$ and $\vec{B} \perp \vec{c}$. For B above 100 mT no $\vec{B}$ dependence was found. The linear increase of T_1^{-1} with T is ascribed to coupling to conduction electrons and is discussed in terms of a local density of states. No diffusion induced T_1^{-1} contribution was observed below 320 K.

Keywords: spin-lattice relaxation, high pressure intercalation, β-radiation detected NMR, electronic properties

INTRODUCTION

High pressure intercalation techniques have made available new stage-1 alkali graphite intercalation compounds (GICs) with highly dense alkali layers[1]. Investigation of the structure of the LiC$_x$ system by X-ray diffraction[2] revealed LiC$_2$ as the most dense compound. It decomposes after pressure release.

Here first results are presented obtained by β-radiation detected nuclear magnetic resonance/relaxation (β-NMR)[3] with the short-lived probe ^{8}Li($T_{1/2}$=0.8s). This in-situ method allows nuclear spin-lattice relaxation (SLR) measurements to be performed in the sample containers of the high-pressure synthesis.

EXPERIMENTAL

The samples were prepared from isotopically pure ^{7}Li metal and highly oriented pyrolythic graphite (HOPG) under 60 kbar pressure at a temperature of 550 K in bronze ampoules. The ^{7}Li enrichment served to prevent parasitic neutron absorption by ^{6}Li besides the ^{7}Li(n,γ)^{8}Li activation process yielding the β-NMR probe ^{8}Li. Two ampoules of 7mm diameter and 6mm length were used in the present measurements. At ambient pressure the decomposition of the LiC_2 phase proceeds via $Li_{11}C_{24}$ ($\equiv LiC_{2.18}$) finally to Li_7C_{24} ($\equiv LiC_{3.4}$) which is stable[2]. In the present measurements the transformation was avoided by keeping the samples in the metallic self-sealing ampoules of the high pressure intercalation synthesis. At most a minor admixture of $LiC_{2.18}$ is to be expected in the samples. A decomposition, which would have been accompanied by a substantial volume increase, can also be excluded on account of the constant volume of the ampoules. For brevity in the following the sample composition will be denoted by LiC_2.

The ^{8}Li probes ($T_{1/2}$ = 0.8 s) are produced by capture of cold polarized neutrons from the ^{7}Li nuclei in the sample. The β-decay radiation of ^{8}Li is asymmetric with respect to the nuclear polarization axis which is parallel to the external magnetic field $\vec{B}$. Any changes of the nuclear polarization due to resonance or relaxation are detected via changes of the β-radiation asymmetry. Detailed descriptions of this method and its application to Li-GICs are given elsewhere[4,5]. Due to the neutron activation of the probe nuclei and the radiation detection of their polarization without radiofrequency irradiation bulk metal samples as well as sealed metal containers may be used. Similar to neutron scattering experiments the amount of required sample material is in the cm^3 range. Thus the statistical accuracy of the data suffered somewhat from the limitation to only two ampoules simultaneously mounted in the spectrometer.

The measurements were done with the β-NMR-spectrometer at the FRJ-2 reactor of the research center Jülich. Spin-relaxation measurements were performed between 4.2 K and 320 K at magnetic fields between 8.2 mT and 1.7 T for the orientations $\vec{B}\|\vec{c}$ and $\vec{B}\perp\vec{c}$ of the HOPG stacking with respect to $\vec{B}$.

RESULTS AND DISCUSSION

Measurements of the time dependence of the ^{8}Li polarization, which showed no deviation from single exponential decay as it is expected for single phase material with equivalent sites, yielded the SLR rate T_1^{-1}. For B above 100 mT, which corresponds to a frequency of 630 kHz, no dependence of T_1^{-1} on $\vec{B}$ is observed and T_1^{-1} increases linearly with T, as shown in Figure 1, according to the law $T_1^{-1} = aT$ with $a = 1.87(5) \times 10^{-3}$ s^{-1}K^{-1}. These SLR features are typical for coupling of the nuclear dipole moment to conduction electrons. The corresponding rate is given by[6]

$$T_1^{-1} = \frac{64\pi^3}{9}(\gamma_n\gamma_e)^2\hbar^3 \,|\langle|\psi(0)|^2\rangle_{E_F}|^2 \,\rho(E_F)^2 \,k_BT \tag{1}$$

where γ_n, γ_e are the gyromagnetic ratios of the probe nucleus and the electron, respectively; $\langle|\psi(0)|^2\rangle_{E_F}$ is the probability density at the site of the probe nucleus averaged over the Fermi surface and $\rho(E_F)$ the density of states at the Fermi level. Thus $\sqrt{a}$ gives access to electronic properties as represented by the product $\langle|\psi(0)|^2\rangle_{E_F}\,\rho(E_F)$ which is sometimes referred to as local density of states (LDOS)[7]. The value for a corresponds to a LDOS of 0.17 eV^{-1} Å^{-3}. For comparison various findings for T_1T of ^{8}Li in GICs and bulk Li are summarized in Table I. It also contains the value for Li adsorbed on a Ru(001) surface as an example for a purely 2D system. Its LDOS lies in the range of the values for the Li-GICs. However, in a comparison of the T_1T values the nature of the substrate or host materials has to be considered.

TABLE I Comparison of $T_1T = a$ values of the SLR rate T_1^{-1} of ^{8}Li in different Li-GICs, Li metal and Li adsorbed on Ru(001).

	T_1T [sK]	reference
Li metal	290	[8]
LiC_2	540	this work
Li/Ru(001)	900	[7]
LiC_{12}	2600	[9]

A more detailed analysis of electronic properties would be possible by comparison with the Knight shift K of the resonance line via the Korringa relation $T_1TK^2\eta = (\hbar/4\pi k_B)(\gamma_n/\gamma_e)^2$ where η accounts for electron-electron interaction ($\eta < 1$) and/or dimensionality effects ($\eta \gg 1$ in low-D electronic systems[10]). However, corresponding ^{7}Li NMR measurements were done after pressure release[11] and there is some doubt whether the same high density phase as in the present case was investigated. The main feature of the ^{7}Li line spectrum is a doublet which was compared with simulations leading to the suggestion that the less dense compound Li_7C_{24} ($LiC_{3.4}$) was formed. Furthermore the ^{7}Li line spectrum narrows with rising T between 250 K and 300 K, which indicates the onset of Li motion

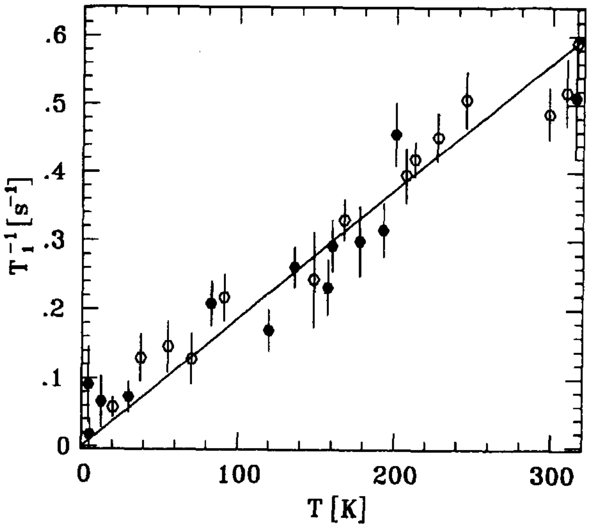

FIGURE 1 Temperature dependence of the SLR rate ^{8}Li in LiC_2 at B= 472 mT for $\vec{B}||\vec{c}$ (○) and $\vec{B} \perp \vec{c}$ (•). The solid line corresponds to T_1T = 540(20) sK.

in close resemblance to the self diffusion in Li metal and the Li-GICs LiC_6 and LiC_{12}. The absence of diffusion induced SLR in the presently investigated denser phase is in accordance with the expected lower concentration of vacancies.

CONCLUSION

In the T range between 4.2 K and 320 K the SLR rate of ^{8}Li in LiC_2 is due to coupling to conduction electrons. The observed law T_1T = *const* gives access to the local density of states. No additional SLR contribution due to diffusion is observed in the considered B and T range in accordance with the conception of a highly dense Li layer with a very low concentration of structural vacancies.

Acknowledgements

This work was supported in parts by the BMBF under HE4HAN.

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