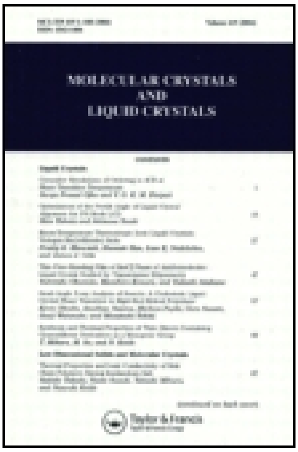

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NMR Study of Lithium Dybutilamine Molybdenum Disulfide Nanocomposite

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Measurements of ^1H and ^7Li Nuclear Magnetic Resonance (NMR) are reported for the nanocomposite formed by the intercalation of lithium and dibutylamine in molybdenum disulfide, $Li_{0.1}[(C_4H_9)_2NH]_yMoS_2$. The temperature dependence NMR lineshapes and spin-lattice relaxation times (T_1) measured exhibit the qualitative features associated with the lithium motions, namely the presence of a line narrowing at 230 K. The ^1H and the ^7Li longitudinal magnetization recovery was found to be non exponential. The T_1 values at each temperature was determined from the fit of a stretched exponential function. An activation energy for the lithium motion $E_a \approx 0.18$ eV was extracted from the ^7Li relaxation data. The dynamical parameters obtained from the ^7Li temperature dependence relaxation data indicate the mobility of the lithium in the nanocompositeis of the same order of magnitude as those obtained in other lithium intercalation compounds.

Keywords Organic-Inorganic Nanocomposite; MoS_2; NMR; Intercalation compound; Nuclear Relaxation

INTRODUCTION

Interest in intercalation compounds derived from lamellar transition metal dichalcogenides for use in solid-state batteries has increased in recent years [1-3]. Many of these layered materials intercalate organic molecules into their galleries, leading to alternative nanostructures. The nanocomposites based on the insertion of lithium and organic species (secondary amines) into molybdenum disulphide are a relatively new class of layered compound that have received special attention [4]. NMR is a well-known experimental technique for the selective study of ionic, atomic and molecular motions in nanostructured materials since it is sensitive to the effects that such motions have on the linewidth and spin-relaxation rates [4-6]. In the present work, we report a proton (^{1}H) and lithium (^{7}Li) NMR lineshape and spin-lattice relaxation investigation of the layered organic-inorganic nanocomposite obtained from the co-intercalation of lithium and dibutylamine (DBA) in molybdenum disulfide, $Li_{0.1}[(C_4H_9)_2NH]_{0.2}MoS_2$.

EXPERIMENTAL

The preparation details of the nanocomposite was described elsewhere [4]. The amine was added to a suspension of exfoliated MoS_2 prepared by treating Li_xMoS_2 with deionized disaered water. The suspension was stirred during 24 h at room temperature and the solid product was separated, washed, dried under vacuum and stored under argon atmosphere. Proton (^{1}H) NMR linewidth and spin-lattice relaxation time (T_1) measurements were carried out on a pulsed NMR spectrometer operating at 36 MHz equipped with a TECMAG NMR-kit. The spin lattice relaxation in the rotating frame were determined by a spin-lock sequence with a lock field $H_1 = 5.2$ G. The ^{7}Li NMR measurements were performed at 155.4 MHz on a Varian-400 MHz *INOVA* spectrometer using a multinuclear wide-line probe.

RESULTS and DISCUSSION

Figure 1 shows the temperature dependence of the linewidth of the central line of the ^{7}Li NMR spectrum. At temperatures below 200 K the line shape is Gaussian and the linewidth is almost constant (~ 7.2 kHz). The Gaussian shape of the central line of the rigid lattice spectra indicates that the broadening results from dipole-dipole interactions, i.e. the interaction of Li with the surrounding atoms (mainly ^{7}Li-^{7}Li and ^{7}Li-^{1}H interactions, where the proton belong from the amine group). At temperatures above 200 K the central line begins to narrow and the shape of the central transition change from Gaussian to Lorentzian. Motional narrowing begin when the rate of the fluctuations (measured by τ_c^{-1}) of either the local dipolar fields or the electric field gradients are comparable to the rigid lattice linewidth (H_{RL}), e.i. when, $\tau_c^{-1} \approx H_{RL}$. Here τ_c is the lithium motional correlation time, $\tau_c = \tau_o \exp(E_a/kT)$ where E_a indicates the activation energy.

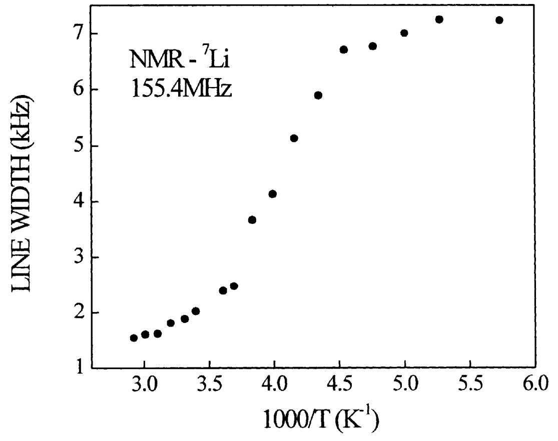

FIGURE 1 Temperature dependence of the ^{7}Li NMR central transition linewidth in $Li_{0.1}$ $[DBA]_y$ MoS_2.

The proton spin-lattice relaxation times T_1 were measured over the temperature range 200 to 430 K. In general, for a spin ½ system, the recovery of the magnetization M_z to its equilibrium value M_{zo} is expected to be a single exponential function of time, yielding a single relaxation time T_1. But for the ^{1}H (I = ½) and the ^{7}Li (I = 3/2) in the $Li_{0.1}$ $[DBA]_yMoS_2$ nanocomposite the time evolution of (M_z - M_{zo}) cannot be adequately fitted by a single exponential or by a superposition of two exponentials. The best description was obtained with a stretched exponential such as the Kohlrausch-Williams-Watts (KWW) function [7,8]. Accordingly, the T_1 values at each temperature were determined by fitting the experimental M_z with a stretched exponential function [8]. The stretch parameter β (with $0< \beta \leq 1$) is directly related to the distribution of T_1 values. The most commonly proposed explanations of the nature of this nonexponential behavior are either a spatially heterogeneous distribution of correlation times where slow and fast processes occur at the same time or an intrinsically nonexponential loss of correlation in a homogeneous system where slow and fast processes occur in series [9]. The KWW stretched exponential have been extensively used in the field of dielectric relaxation spectroscopy but has been little exploited in the field of NMR [13 and cited references].

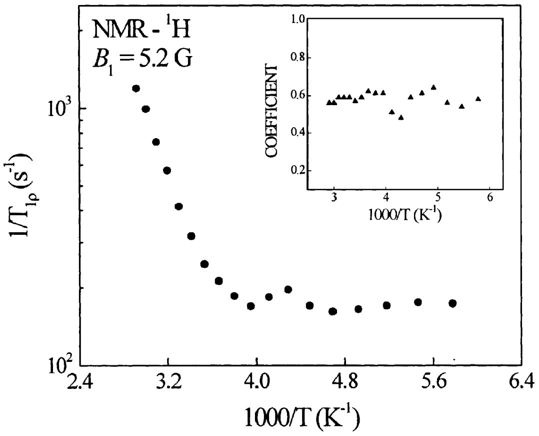

FIGURE 2 Temperature dependence of the ¹H spin-relaxation rates in the rotating frame ($T_{1\rho}^{-1}$) in $Li_{0.1}$ [DBA]$_y$ MoS_2 measured at the Larmor frequency ω_o = 36 MHz and a lock field H_l = 5.2 G. Insert: temperature dependence of the stretch parameter β in Eq. [1].

The proton spin-lattice relaxation time T_1 in the $Li_{0.1}$ [DBA]$_y$$MoS_2$ nanocomposite was found to be constant (T_1 ~ 90 ms) from 200 to 260 K. Above 260 K the relaxation time decrease with increasing temperature, until a value of T_1 ~ 40 ms is attained at approximately 340 K. Any relaxation time minima were observed in the temperature range investigated, which is limited by the chemical stabilization of the nanocomposite. The position of the relaxation time minimum in an Arrhenius plot of T_1 indicates the temperature at which the motional correlation time τ_c is comparable to the reciprocal of the ¹H Larmor frequency in the laboratory frame ($\tau_c \sim 1/\omega_o \approx 10^{-9}$ s). The absence of a relaxation time minimum indicate that the proton rate of motion is lower than this frequency. Measurements of the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) were undertaken between 173 K and 340 K. In this case, the position of a $T_{1\rho}$ minimum (or equivalently, a relaxation rate maximum) indicates the temperature at which τ_c is comparable to the reciprocal of the ^{1}H frequency in the lock field H_l ($\tau_c \sim (2\omega_1)^{-1} = (2\gamma H_l)^{-1} \approx 10^{-5}$ s, where γ is the proton gyromagnetic ratio).

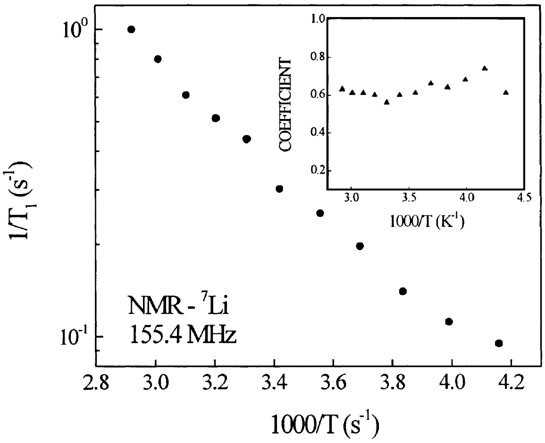

FIGURE 3 Temperature dependence of the ^{7}Li spin-relaxation rates (T_1^{-1}) in $Li_{0.1}$ $[DBA]_y MoS_2$. Insert: temperature dependence of the stretch parameter β in Eq. [1].

Figure 2 shows the temperature dependence of the proton spin-lattice relaxation rates in the rotating frame ($T_{1\rho}^{-1}$) of the nanocomposite $Li_{0.1}$ $[DBA]_yMoS_2$. The magnetization recovery toward equilibrium was found to be nonexponential and was analyzed with the stretched exponential Eq. [1]. The insert of Fig. 2 shows that the stretch parameter β is roughly constant with the temperature, indicating that the fitting procedure of the magnetization recovery was consistent. The data in Fig. 2 display any relaxation rate maxima. Above 260 K, $T_{1\rho}^{-1}$ increases with increasing temperature. The activation energy calculated from the linear slope of the ^{1}H $T_{1\rho}^{-1}$ curve is $E_a \approx 0.23$ eV. The mechanism responsible for the proton relaxation in this nanocomposite is the random fluctuations of the dipole – dipole interaction caused by the amine motions, and the modulation of the H – Li distances between a proton and the lithium.

Figure 3 shows the temperature dependence of the ^{7}Li spin-lattice relaxation rates in the laboratory frame (T_1^{-1}) of the nanocomposite $Li_{0.1}[DBA]_yMoS_2$. Above 250 K there is a increase of one order magnitude (from $T_1^{-1} \approx 0.1$ s^{-1} to 1.0 s^{-1}). The insert of Fig. 3 shows that the stretch parameter β is constant in the temperature range investigated, with $\beta \approx 0.6$. It should be noted that a value of $\beta = 1$ reflects an infinitely narrow distribution (in such case Eq. [1] becomes a single exponential) and a value of $\beta = 0$ reflects an infinitely broad distribution of correlation times. No relaxation rate maximum was observed in Fig. 3. The activation energy for the lithium motion extracted from the linear slope of the Arrhenius plot of the T_1^{-1} data (Fig. 3) is $E_a \approx 0.18$ eV, in good agreement with the value reported for the diethylamine nanocomposite $Li_{0.1}[(C_2H_5)_2NH]_{0.2}MoS_2$ (0.18 eV) [10] and the values reported for layered compounds and transition metal dichalcogenides studied by ^{7}Li NMR, which lies in the range 0.1 and 0.3 eV [4].

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