Nuclear spin relaxation and correlated diffusion of impurities
K. Becker

To cite this version:

HAL Id: jpa-00220101
https://hal.archives-ouvertes.fr/jpa-00220101
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Nuclear spin relaxation and correlated diffusion of impurities

K. D. Becker
Lehrstuhl für Physikalische Chemie, Ruhr-Universität Bochum, D-4630 Bochum, F.R.G.

Résumé. — A partir des expériences des largeurs des raies de la RMN sur la diffusion des ions Na\(^+\) et Li\(^+\) dans AgBr, nous avons calculé les enthalpies d’activation de la diffusion

\[ h(\text{Na}^+) = (1.21 \pm 0.05) \text{ eV} \quad \text{et} \quad h(\text{Li}^+) = (0.88 \pm 0.04) \text{ eV}. \]

Ces valeurs indiquent des effets de corrélation dans la diffusion des impuretés, si l’on compare les résultats de la RMN avec ceux de la conductibilité et de la diffusion de tracer. La diffusion des ions Na\(^+\) se comporte presque parfaitement comme un random walk. Par contre, les ions Li\(^+\) sont démontrés être des impuretés diffusant très rapidement dans AgBr avec des fréquences de saut des lacunes plus hautes que celles des cations du réseau.

Abstract. — From NMR line width experiments on the diffusion of Na\(^+\) and Li\(^+\) ions in AgBr activation enthalpies of \( h(\text{Na}^+) = (1.21 \pm 0.05) \text{ eV} \) and \( h(\text{Li}^+) = (0.88 \pm 0.04) \text{ eV} \) are deduced for NMR correlation times. Correlation effects in impurity diffusion are inferred from a comparison of the NMR data to results from conductivity and tracer diffusion. Na\(^+\) ions are found to perform an almost perfect random walk. In contrast, Li\(^+\) ions are shown to be fast diffusing impurities in AgBr with vacancy jump frequencies larger than those of the host cations.

1. Introduction. — The study of correlation effects is a most important means for obtaining information on details of atomic migration processes in solids. In ionic crystals for the analysis of these effects usually dual experiments are performed on the macroscopic transport of mass and charge of the atomic species under consideration. Common to this class of experiments is that the correlation effects they monitor, solely are due to spatial correlation of the atomic motion [1]. In contradistinction to experiments on macroscopic transport, nuclear spin relaxation is influenced not only by spatial correlations but also by the temporal correlation of the atomic jumps. Hence, different aspects of correlation are probed. Comparison of NMR data to results obtained from tracer and/or electrical conductivity measurements therefore in principle offers the possibility to extract information concerning these effects.

It is the purpose of this paper to demonstrate that NMR furnishes a valuable tool also for the investigation of correlation effects in impurity diffusion. In contrast with NMR work on the diffusion of lattice atoms in pure crystals, the method presented here makes use of dynamic quadrupolar nuclear interactions caused by the impurities. Until now, this method has been applied to ionic crystals only [2-5], though not necessarily limited to them. The examples presented here are concerned with diffusion and correlation effects of homovalent Na\(^+\) and Li\(^+\) ions in silver bromide; the possibility of double doping with heterovalent impurities will also be considered.

2. Theory. — Relaxation of nuclei with spin \( I \geq 1 \) possessing an electric quadrupole moment \( Q \) often is dominated by interactions between \( Q \) and gradients of the innercrystalline electric field (EFG) created by impurities. Diffusion of the impurities renders the EFGs time dependent and thus can cause relaxation of the nuclear spin system. Quantities accessible to NMR experiments then are determined by the spectral density functions \( J^{(H)}(\omega) \) of fluctuating EFG functions. The quadrupolar line shape function of the nuclear absorption signal is given by the superposition of a central and a satellite part. The central component is given by a Lorentzian with a width [4, 5]

\[ \Delta \omega = \frac{1}{6 \sqrt{3}} \left( \frac{eQ}{\hbar} \right)^2 \left[ J^{(1)}(\omega_\text{L}) + J^{(2)}(2 \omega_\text{L}) \right] \]

\( \omega_\text{L} \) is the Larmor frequency in the experiment. In polycrystalline samples, satellite signals of nuclei extremely sensitive to quadrupolar interactions, usually are broadened beyond detection [6]. The experimentally observed line width is then given by

\[ \Delta \omega = \Delta \omega_5^\text{q} + \Delta \omega_\text{d}. \]

The width \( \Delta \omega_\text{d} \) of the line shape resulting from additional dipolar interactions can be obtained from experiments on crystals not doped with the impurity under consideration.

Focusing now on impurity diffusion by means of a vacancy mechanism, spectral densities will depend...
on various jump frequencies \( w \), characteristic of vacancy exchange with the impurity and with solvent atoms in the vicinity of the impurity. Though more complex models [7] may be used in the calculation of spectral densities, we will restrict ourselves to a discussion involving only two frequencies \( w_2 \) and \( w_0 \), for vacancy exchange with the solute and with solvent, respectively.

Following the impurity motion in time, reveals the fact that the impurity jumps do not occur at random. After a first exchange with a vacancy, there will be a considerable chance for further exchanges of the impurity with this same vacancy before the vacancy finally diffuses away. Most important in the present context is that, spin relaxation is not influenced by the high frequency and highly correlated motion of the impurity and with impurity. For NMR the impurity migration thus can be represented by a random walk of encounters [8] characterized by particle displacements \( l_j \) occurring with probabilities \( P(l_j) \).

In the two frequency model these \( P(l_j) \) solely depend on the ratio \( (w_2/w_0) = x \) and can be obtained from a Monte-Carlo simulation of the impurity migration. With knowledge of the \( x \)-dependent probability distributions, spectral densities \( J_{NMR}(\omega) \) can be calculated using an extension due to Wolf [8] of Torrey's theory. Here \( \tau_{NMR} \) is the time characteristic of fluctuations of nuclear quadrupole interaction.

Since only those encounters are effective in relaxation which result in a non zero displacement, \( l > 0 \), the following relation holds between the mean jump frequency \( v \) of the impurity and the frequency \( \nu_{NMR} = \tau_{NMR}^{-1} : \)

\[
\nu_{NMR} = v f_{NMR} = \frac{12 [V]}{w_2} \frac{1 - P(0)}{Z(0)}. \tag{3}
\]

Here \([V]\) is the concentration of the vacancies, \( P(0) \) is the probability for the occurrence of an encounter with displacement \( l = 0 \), \( Z(0) \) is the average number of impurity jumps per encounter, which can also be obtained from Monte-Carlo simulations. A calculation of \( f_{NMR}(x) \), the results of which are given in [4], shows that correlation effects in NMR can be quite large for fast diffusing impurities.

3. Results and discussion. — Diffusion of Na\(^+\) in AgBr. — Typical results for temperature dependent measurements on the width \( \Delta B \) of nuclear absorption signals are shown in figure 1 for the diffusion of Na\(^+\) ions in AgBr. The data for the absorption of \( ^{81}\)Br in pure and doped material clearly exhibit the proportionality of \( \Delta B \) to dopant concentration, required by (1) and (2). NMR jump frequencies of the Na\(^+\) ions were obtained by the procedure indicated above; more details may be found in [4]. Defining an NMR diffusion coefficient \( D_{NMR} = \frac{1}{2} \nu_{NMR} d^2 \), NMR data may be compared to results from tracer experiments \( (D') \). For such a comparison with recent tracer experiments [9], shown in figure 2, \( d = \frac{1}{2} a_0 \sqrt{2} \) (\( a_0 \) lattice constant) was assumed as length of the Na\(^+\) jumps.

Fig. 1. — Line width \( \Delta B \) of the absorption of \( ^{81}\)Br in pure and NaBr doped AgBr; \( x(\text{NaBr}): 1 \times 10^{-2} (\bullet), 5 \times 10^{-2} (\bullet), 1 \times 10^{-2} (\bigcirc), 1 \times 10^{-3} (\bigtriangleup) \), \( \nu_R = 16 \text{ MHz} \).

Fig. 2. — Tracer (○, [9]) and NMR (●) diffusion coefficients of Na\(^+\) ions in AgBr.

It is satisfying that also the NMR data display the curvature in the Arrhenius plot characteristic of the well known high temperature transport anomaly in AgBr [9-11]. In the low temperature range \( \nu_{NMR} \) can be described by a preexponential \( \nu_{NMR}^0 = 1 \times 10^{18} \) and an activation enthalpy of \( (1.21 \pm 0.05) \text{ eV} \). The apparent activation enthalpy increases to 1.5 eV near the melting point. From the good agreement between both sets of data, from a comparison of \( f_{NMR} \) and \( f' \) made in [4], \( f_{NMR} = f' = 1 \) is deduced, since \( D_{NMR}/D' = f_{NMR}/f' \). This implies \( w_2 < w_0 \) and that the sodium ions on the average perform only one jump per encounter. A result which corresponds to the fact that the diffusion of Na\(^+\) is slow when compared to vacancy diffusion of the host cations.

Diffusion of Li\(^+\) in AgBr. — In contrast to sodium, lithium ions diffuse faster than silver ions. This is shown in figure 3, where \( \nu_{NMR}(\text{Li}^+) \) is compared to the vacancy jump frequency of Ag\(^+\), obtained from conductivity work [10]. In the whole temperature range investigated, \( R = (\nu_{NMR}(\text{Li}^+))(\text{Ag}^+) \approx 2 \) is observed. Also in the case of Li\(^+\) diffusion the Arrehen-
NUCLEAR SPIN RELAXATION AND CORRELATED DIFFUSION OF IMPURITIES

Fig. 3. — NMR jump frequency of Li$^+$ ions (●) and vacancy jump frequency of Ag$^+$ ions in AgBr.

The Arrhenius plot exhibits pronounced curvature. In the low temperature portion $v_{\text{NMR}}(\text{Li}^+)$ can be described by an activation enthalpy of $(0.88 \pm 0.04)$ eV.

It is easy to show that in the two frequency model $R = x f_{\text{NMR}}^2(x)$ holds. Using $f_{\text{NMR}}^2(x)$ from [4], it is concluded that Li$^+$ ions jump much more rapidly than Ag$^+$ ions jump by means of vacancies. A large value $x = w_2/w_0$ of order 10 is indicated by this analysis in the framework of the two frequency model. This result is consistent with the above value for the activation enthalpy of $v_{\text{NMR}}(\text{Li}^+)$, which, as a consequence of the large NMR correlation effects for fast diffusing impurities, is equal to the activation enthalpy for vacancy diffusion of Ag$^+$ ions [10, 11].

DISCUSSION

Question. — R. J. Friauf.

Earlier ionic conductivity measurements show that Cu$^+$ occupies an interstitial position and moves very rapidly in both AgCl and AgBr. This allows one to speculate as to whether the rapid motion of Li$^+$ may involve some kind of interstitial motion, even though your last discussion provides some evidence to the contrary.

Reply. — K. D. Becker.

Neither the frequencies of direct interstitial nor those of interstitialcy processes can be influenced by changes in the concentration of cation vacancies. Further evidence for vacancy migration of Li$^+$ is given by the curvature of the Arrhenius plot (Fig. 3), which closely follows the anomalous increase in vacancy concentration.

Question. — O. Kanert.

Have you done relaxation time measurements on $^{79}$Br or $^{81}$Br, too?

Reply. — K. D. Becker.

Impurity induced quadrupolar relaxation effects also have been observed in measurements of the longitudinal relaxation time. However, $T_1$ of $^{81}$Br in pure AgBr is already rather short; the relaxation times down to about 5 μs encountered in doped AgBr are more easily measured by wide line (cw) experiments ($\nu_L = 16$ MHz).

References