

Motional Narrowing of Nuclear Magnetic-Resonance Lines in Manganese-Doped Lithium Fluoride*

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Nuclear magnetic-resonance experiments have been performed between 25 and 550°C in LiF powder doped with manganese. Motional narrowing of the Li⁷ resonance line occurred somewhat below 400°C. Resonance absorption lines were not observable in the temperature range 200–390°C, probably because an effective loss of paramagnetic relaxation centers increased the spin-lattice relaxation time. Electron spin-resonance experiments verified that the paramagnetic manganese does cluster upon heating above 200°C. A method of analysis is developed which eliminates errors due to constant linewidth contributions in the analysis of motional narrowing data in terms of diffusion activation energies. The activation energy for motion of Li ion vacancies in LiF is found to be 0.74 eV.

I. INTRODUCTION

MOTIONAL narrowing of nuclear magnetic-resonance lines has been used to investigate extrinsic diffusion in several doped ionic crystals. Examples include¹ LiBr where vacancies present on Li sites gave rise to extrinsic Li-ion diffusion, and^{2,3} CaF₂ where F ions were seen to diffuse. In the present study, motional narrowing is observed in manganese-doped LiF powder. The substitution of Mn²⁺ ions for Li⁺ ions in LiF gives rise to an equal number of Li-ion vacancies to maintain charge neutrality. For this reason, it is possible to interpret motional narrowing in this system in terms of the diffusion of Li-ion vacancies.

II. EXPERIMENTAL TECHNIQUES

Powdered LiF samples were prepared by precipitation with NH₄F from an aqueous solution of LiCl containing 0.1% MnCl₂. They were subsequently filtered, washed, and then dried at 100°C for a short time. The Li⁷ nuclear magnetic-resonance absorption line was observed at 7.5 Mc/sec using a modified Varian wide-line spectrometer. Experiments were performed between 25 and 550°C by inserting an air-cooled high-temperature Dewar in the Varian probe.

III. METHOD OF DATA ANALYSIS

To date, the analysis of motional narrowing curves to give diffusion coefficients has been only moderately successful. In metallic aluminum⁴ and lithium,^{5,6} experimental activation energies for diffusion have varied

from values obtained by other techniques^{7–9} by up to 30%. This is due both to changes in lineshape and constant contributions to the linewidth, which make data analysis uncertain.

A method has been developed which enables analysis of motional narrowing data to produce accurate values of diffusion activation energies. It eliminates errors due to any constant contributions to the linewidth, including magnetic-field inhomogeneities, and is applicable in temperature regions where the lineshape is nearly constant.

Since narrowed lines are nearly Lorentzian,¹⁰ the actual dipolar linewidth δH_d can be related to the diffusion coefficient D by the relation

$$\delta H_d = C\delta H_0 D^{-1} = A \exp(E/kT), \quad (1)$$

where E is the activation energy for motion of Li-ion vacancies. The constant A contains the concentration of vacancies in the system and the factor relating the linewidth to $(1/T_2)$. The relation between the measured line width δH_m and the actual dipolar linewidth can be written

$$\delta H_m = a\delta H_d + b\delta H_1, \quad (2)$$

where δH_1 is a constant.

One of the methods of data analysis that has been used by others consists of plotting $\ln\delta H_m$ versus $1/T$ and equating the slope of the curve to E/k . If, however, a constant addition to the line width is present such as given in (2), the slope S obtained in this manner is not E/k but rather

$$S = \frac{d \ln \delta H_m}{d(1/T)} = \frac{E}{k} \frac{1}{[1 + (b\delta H_1/aA)e^{-E/kT}]}. \quad (3)$$

Equation (3) shows that S becomes smaller than E/k at higher temperatures, which is the region of interest in the present case.

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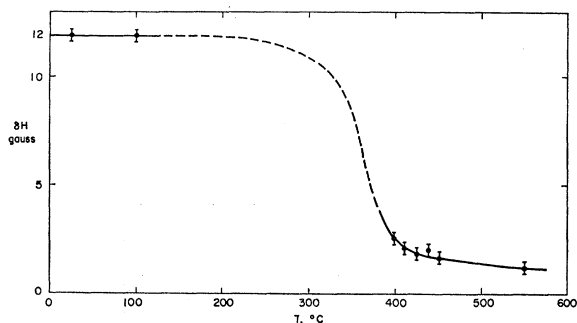


FIG. 1. Linewidth of Li^7 resonance line in Mn-doped LiF as a function of temperature.

If, however, δH_m is first differentiated with respect to $1/T$, followed by taking the logarithm of this derivative, we have

$$\ln \Delta \equiv \ln \frac{d\delta H_m}{d(1/T)} = \text{const} + \frac{E}{kT}. \quad (4)$$

The slope S of a plot of $\ln \Delta$ versus $1/T$ will now yield the true value of E/k , independent¹¹ of δH_1 . This analysis is easily performed, since Δ can be evaluated at several temperatures on a plot of the experimental data for δH_m versus $1/T$.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The temperature variation of the observed linewidth, defined as the width in gauss between the points of maximum and minimum slope, is given in Fig. 1. The limits of error shown were determined from estimates of the experimental accuracy in determining the linewidth and from the variations between values obtained from several experimental measurements at the same temperature. The room-temperature values of linewidth may be compared with the half max-min linewidth of about 6 G given by Chang *et al.*^{12,13} in similar samples at 77°K. Nuclear-resonance lines of F^{19} in this material narrowed by about 25% in the same temperature range in which the Li^7 narrowed.

¹¹ It should be noted that if we include the bilinear term in the expansion of Eq. (2), $(\partial \delta H_m / \partial H_1)$, nothing is changed in the result except the constant a .

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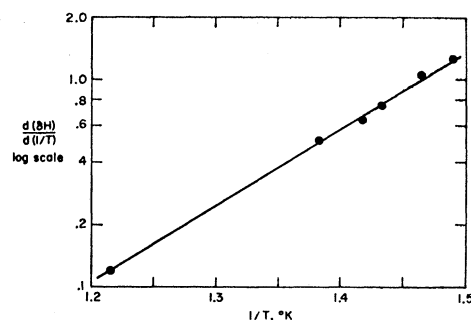


FIG. 2. Plot of $\ln[d\delta H/d(1/T)]$ versus $1/T$ for the data of Fig. 1, which yields activation energy of 0.74 eV. (Note added in proof. The scale on abscissa and ordinate should contain a factor of 10^3 .)

Absorption lines could not be obtained in the temperature interval 200–390°C because of a long spin-lattice relaxation time. This was probably caused by an effective loss of paramagnetic-relaxation centers from the system. Electron spin-resonance experiments were performed, indicating that the manganese ions are uniformly distributed in the lattice at room temperature. After heating the samples for short times above 200°C, the electron spin-resonance line observed at room temperature loses its hyperfine structure due to a strong exchange interaction. This is probably due to clustering of Mn in the Li sublattice, similar to the clustering observed by Jennings¹⁴ in Mn-doped LiCl single crystals. The electron spin-resonance spectra before heating are very similar to those observed by Chang *et al.*^{12,13}

The analysis described in Sec. III has been performed on the high-temperature data of Fig. 1. The resulting straight line, shown in Fig. 2, yields an activation energy of 0.74 eV, with a precision of about 10%. This is in good agreement with the activation energies obtained in the extrinsic region by investigators using other techniques; electrical-conductivity results¹⁵ have given $E=0.65$ eV and spin-echo experiments in single crystals¹⁶ have given 0.71 eV. By comparison of the present data with the results of electrical conductivity experiments,¹⁵ it can be determined that the vacancy concentration in the present work is about 5×10^{-5} .

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