The Effect of Lattice Vacancies on the NQR Parameters *,**

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Z. Naturforsch. **41 a,** 378–381 (1986); revised version received September 19, 1985

Lattice vacancy effects on NQR parameters such as the transition frequency (ν_Q), the spin-lattice relaxation time (T_1), and the linewidth ($\Delta\nu$) are studied, and expressions are proposed to describe their temperature behaviour. These expressions are applied to analyse the case of solid chlorine and values are derived for the energy and entropy associated with the creation of a vacancy and its migration energy.

Introduction

Lattice vacancies are thermally activated [1], and their effect on the temperature dependence of ν_Q, T_1 and $\Delta\nu$ poses a problem which hitherto has not been studied. It is our purpose to study this problem systematically. The simplest case to deal with is that of molecular crystals since for these crystals there are, to a good approximation, two main contributions to the electric field gradient tensor at the site of the resonant nucleus (EFG): one intramolecular ($\mathrm{EFG}_{\mathrm{mol}}$) and the other intermolecular ($\mathrm{EFG}_{\mathrm{cryst}}$). In general the $\mathrm{EFG}_{\mathrm{cryst}}$ is less than 10% of the $\mathrm{EFG}_{\mathrm{mol}}$ [2], and it is clear that only the $\mathrm{EFG}_{\mathrm{cryst}}$ will be affected by the presence of vacancies. It is through the analysis of the $\mathrm{EFG}_{\mathrm{cryst}}$, i.e. of its average value and of its fluctuations, that the effect of vacancies on ν_Q, T_1 and $\Delta\nu$ may be analysed. The expressions derived are successfully applied to the analysis of th above quantities in solid chlorine, and values are deduced for ε_f, s_f and ε_m.

Theory

Effects of Vacancies on ν_Q vs. T

The lattice contribution to the EFG may be taken into account in the expression describing ν_Q vs. T as [3–5]

$$\nu_Q = \nu_0 \left[1 - \frac{31h}{16\pi^2} \sum_i \frac{1}{I_i \nu_i} \coth \frac{h\nu_i}{2kT} \right] + \nu_c(T), \tag{1}$$

where ν_0 corresponds to ν_Q in a rigid isolated molecule, I_i is the moment of inertia associated with the normal mode of vibration whose frequency is ν_i [6], and $\nu_c(T)$ represents the lattice contribution to the EFG at the site of the resonant nucleus. The EFG asymmetry parameter is assumed to be zero; the extension to include it is straightforward. Let us consider a particular resonant nucleus, belonging to a molecule located at a given crystalline site, and let ν_{ci} be the contribution of crystalline site i, when occupied, to the ν_Q of our particular resonant nucleus. Assuming that the total crystalline contribution is obtained by adding those from all sites in the crystal, we have

$$\nu_c^0 = \sum_i \nu_{ci}, \tag{2}$$

where ν_c^0 is the lattice contribution when no vacancies are present. However, if vacanices are present some of the i sites will be empty. Two limiting cases are of interest: either vacancies migrate very slowly or very fast, as compared to ν_c^0. In the first case, the vacancies are essentially static and they behave as crystalline defects that will broaden the absorption line beyond detection [7]. In the second case vacancies migrate and, even though

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* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

** This research was partially supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and by Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR).

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their existence produces broadening of the absorption line, their fast motion induces a line narrowing effect. In this second case it has only physical sense to speak of the probability that site i is occupied or not. This probability, P_i, is given by

$$P_i = 1 - n_v = 1 - \exp(s_f/k)\exp(-\varepsilon_f/kT), \quad (3)$$

where n_v is the vacancy concentration [1]. It is important to point out that we are assuming a small enough vacancy concentration for neglecting vacancy-vacancy interaction, and also to neglect formation of vacancy clusters [1]. It may be mentioned that the typical vacancy concentration near the melting point is just about a few per cent [1], which justifies the above assumption. Therefore, in this second case the lattice contribution v_c^0 will be altered by the presence of vacancies to

$$v_c(T) = \sum P_i v_{ci} = v_c^0 [1 - \exp(s_f/k)\exp(-\varepsilon_f/kT)],$$

since P_i does not depend on the particular site i, being the same for them all. Equation (4) predicts an exponential behaviour which superposes the normal one given by (1) [3–6, 8]. It should be mentioned that all relaxation effects associated to vacancies [9] have been neglected; the main consequence of this will be to produce a slightly undervalued formation entropy.

Effect of Vacancies on T_1 vs. T

The crystalline contribution to the EFG will undergo changes produced by the motion of the vacancies. The spin-lattice relaxation rate is given by [8]

$$\frac{1}{T_1} = 2(W_1 + W_2) = \frac{e^2 Q^2}{6\hbar^2}[J_1(\omega_Q) + \tfrac{1}{4} J_2(\omega_Q)], \quad (5)$$

where

$$W_1 = \frac{e^2 Q^2}{12\hbar^2} \int_{-\infty}^{\infty} \langle V_{\pm1}(t)\, V_{\pm1}^*(t+\tau)\rangle \exp(-i\,\omega_Q \tau)\,d\tau, \quad (6)$$

$$W_2 = \frac{e^2 Q^2}{48\hbar^2} \int_{-\infty}^{\infty} \langle V_{\pm2}(t)\, V_{\pm2}^*(t+\tau)\rangle \exp(-i\,\omega_Q t)\,d\tau. \quad (7)$$

J_1 and J_2 are the Fourier transforms of the correlation functions of $V_{\pm1}$ and $V_{\pm2}$, respectively, which in turn are the lattice contribution to the EFG components. Following Torrey [10], the resonant nucleus of interest may be considered as fixed, while the vacancies migrate through the lattice jumping an average distance l per jump with a frequency $1/\tau_c$ (τ_c being the correlation time for vacancy motion, or in another words its average residence time at a crystalline lattice site). Considering a vacancy as an additional electric charge, βe (β being a correction factor) and letting a be the minimum distance a vacancy may approach the resonant nucleus, J_1 and J_2 may be written as

$$J_1(\omega_Q) = \frac{1}{4} J_2(\omega_Q) = \frac{16\pi\,\tau_c\, n_v}{15 l^2 a^3 V}(3\beta e)^2$$

$$\cdot \int_{-\infty}^{\infty} J_{3/2}^2(kx) \frac{1 - \dfrac{\sin x}{x}}{\left(\dfrac{\omega_Q \tau_c}{2}\right)^2 + \left(1 - \dfrac{\sin x}{x}\right)^2} \frac{dx}{x}, \quad (8)$$

where $J_{3/2}$ is a Bessel function, $k = a/l$ and V is the volume associated to the primitive cell. Considering $\sin x/x \ll 1$, the spin-lattice relaxation rate due to vacancies migration, $1/T_{1v}$, may be written as

$$\frac{1}{T_{1v}} = \left(\frac{\beta e^2 q Q}{\hbar}\right)^2 \frac{16\pi}{65 V} \frac{n_v \tau_c}{1 + \left(\dfrac{\omega_Q \tau_c}{2}\right)^2}$$

$$\cdot \left[1 + k' \frac{1 - (\omega_Q \tau_c/2)^2}{1 + (\omega_Q \tau_c/2)^2}\right], \quad (9)$$

where

$$k' = \frac{1}{16 k^3} - \frac{3}{4k} + 1. \quad (10)$$

v_c may be estimated [1] as the number of times a vacancy tries to jump times the probability of a successful jump, i.e.

$$\tau_c = \frac{F}{v_l}\exp(-s_m/k)\exp(\varepsilon_m/kT), \quad (11)$$

where F is the number of places a vacancy may jump to, v_l is a typical lattice frequency, and s_m is the entropy associated to the migration of a vacancy. Two limiting cases which are of interest may occur in (9):

$$\omega_Q \tau_c \ll 1, \quad \frac{1}{T_{1v}} = A \exp\left(-\frac{\varepsilon_f - \varepsilon_m}{kT}\right), \quad (12)$$

$$\omega_Q \tau_c \gg 1, \quad \frac{1}{T_{1v}}\; B \exp\left(-\frac{\varepsilon_f + \varepsilon_m}{kT}\right), \quad (13)$$

where A and B are temperature independent constants which may easily be derived from (9).

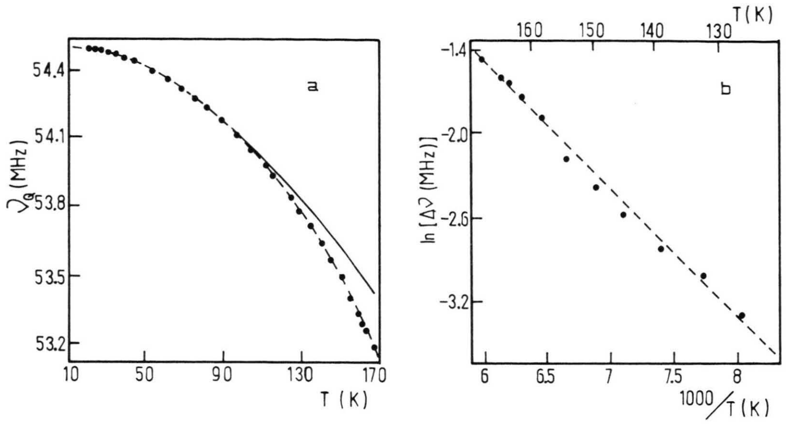

Fig. 1. a) Circles indicate ν_Q vs. T data [14]. Dashed line is ν_Q evaluated including vacancies, as indicated in text. The agreement between theory and experiment is excellent. Solid line corresponds to ν_Q, where the vacancy effect has been neglected. – b) $\Delta\nu$ indicates the difference between the solid and the dashed lines in a). The linear behaviour indicates that $\Delta\nu$ exhibits an exponential dependence on inverse temperature. The circles are derived from the solid line minus the data shown in a).

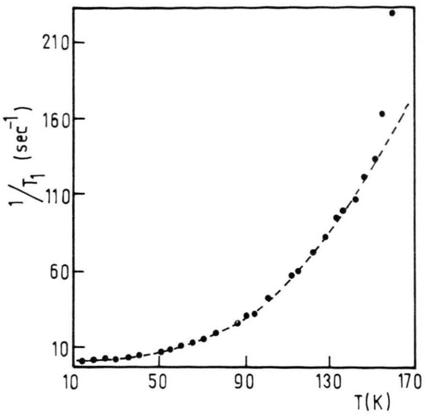

Fig. 2. Circles indicate $1/T_1$ vs. T data [17]. The dashed line corresponds to values generated including vacancies effect. The agreement is excellent, except for the last two points which manifest probably the appearance of an additional relaxation mechanism connected to pre-melting effects.

Therefore the total spin-lattice relaxation rate when vacancies are present is

$$\frac{1}{T_1} = CT^2 + \frac{1}{T_{1\mathrm{v}}}. \tag{14}$$

The first term on the r.h.s. takes into account the standard high temperature Raman process [11, 12].

Effect of Vacancies on the Linewidth

As mentioned above while discussing the effect of vacancies on ν_Q vs. T, there ar two limiting cases depending upon $\nu_c^0 \tau_c \gg 1$ or $\nu_c^0 \tau_c \ll 1$. In the first limit, vacancies are essentially static defects whose effect is to increase inhomogeneously the linewidth and produce the fade-out of the absorption signal. Assuming a low vacancy concentration (which is the general case) and following Stoneham [7], it may be shown that the line shape second moment $\overline{(\Delta\nu)_\mathrm{v}^2}$ is given by

$$\overline{(\Delta\nu)_\mathrm{v}^2} = \left(\frac{\nu_c^0}{G}\right)^2 n_\mathrm{v} = \left(\frac{\nu_c^0}{G}\right)^2 \exp(s_\mathrm{f}/k)\exp(-\varepsilon_\mathrm{f}/kT), \tag{15}$$

where G is a factor of the order of unity, roughly indicating the number of first-neighbour molecules to the resonant nucleus.

In the second limit, $\nu_c^0 \tau_c \ll 1$, the fast vacancy migration produces a line narrowing according to (15) [13], given by the relation

$$\begin{aligned} \Delta\nu_\mathrm{v} &= \left(\frac{\nu_c^0}{G}\right)^2 n_\mathrm{v}\,\tau_c \\ &= \left(\frac{\nu_c^0}{G}\right)^2 \frac{F}{\nu_l} \exp\left(\frac{s_\mathrm{f} - s_\mathrm{m}}{k}\right) \exp\left(-\frac{\varepsilon_\mathrm{f} - \varepsilon_\mathrm{m}}{kT}\right) \end{aligned} \tag{16}$$

which predicts an exponential behaviour of the linewidth.

Application to ν_Q, T_1 and $\Delta\nu$ in Solid Chlorine

Transition Frequency

ν_Q vs. T data were reported by Nakamura and Chihara [14], and it has recently been shown [15] that a sudden departure in the temperature dependence of ν_Q occurs for $T \geqq 120$ K; it was also found that $\nu_c^0 = 11.609$ MHz. Since the absorption line is observed up to, essentially, the melting point with no noticeable broadening, it is concluded that vacancies move fast as compared to ν_c^0, and therefore (4) applies. Using (4) to explain the sudden departure mentioned above [15] it is found that $s_\mathrm{f} = 1.5$ k and $\varepsilon_\mathrm{f} = 7.46$ kJ mol^{-1} K^{-1}.

These values produce an excellent fit to the ν_Q vs. T data as shown in Figure 1. It may be added that these values agree with those found from specific heat analysis [16].

Spin-Lattice Relaxation Time

To analyse T_1 vs. T data [17], (14) is used with $1/T_{1\mathrm{v}}$ given by (12). The values deduced for $C = (2.56 \pm 0.19) \cdot 10^{-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-2}$, $A = (1830 \pm 250)\,\mathrm{s}^{-1}$ and $\varepsilon_\mathrm{m} = 3.43 \pm 0.30)\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$, are very reasonable. Figure 2 shows the excellent agreement achieved between theory and experiment. The value deduced for ε_m indicates that, according to what was mentioned above, as soon as a vacancy is created it will move through the crystal with great easiness. The departure of the last two points in Fig. 2 may be due to pre-melting effects.

Linewidth

As mentioned above, the absorption line does not broaden noticeable up to the melting point [14]. This indicates that (16) applies, and substituting the values for ν_c^0, s_f, ε_f and ε_m mentioned above, and assuming $s_\mathrm{m} = 1.5\,\mathrm{k}$, $G = 4$ and $F = 12$ it is found that $\Delta\nu_\mathrm{v} = 60\exp(-487/T)$ Hz, which at the melting temperature takes a value of 4 Hz, indicating therefore that $\Delta\nu_\mathrm{v}$ contributes negligibly to the linewidth.

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