

## IRREVERSIBILITY OF NMR SIGNAL PASSAGE THROUGH A WEAK FIELD AND THE SPIN-LATTICE RELAXATION MECHANISM IN MOLECULAR CRYSTALS

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It was reported in [1] that Pound's experiment [2] with a naphthalene crystal yielded a negative result. We recall that Pound's experiment established the adiabatic invariance of the magnetization of the nuclear spin system in a crystal lattice under the condition

$$T_2 \ll \tau \ll T_1, \quad (1)$$

where  $\tau$  is the characteristic time (duration) of the experiment.

Pound's and a number of other experiments were theoretically analyzed in detail in the same papers; they served as the material for introducing the concept of spin temperature.

Since there are no reasons for reviewing these papers, we advance the hypothesis that the negative result is due to violation of condition (1), or more accurately to the fact that  $T_1$  is a function of the magnetic field, and is large ( $\sim 30$  min) in strong fields ( $\sim 10$  kG) and small ( $\sim 1$  sec) in weak ones ( $\sim 1$  G).

Tentative measurements have made it possible to establish qualitatively the character of the  $T_1(H)$  dependence. The sample was moved out of a field  $H_0 = 9400$  G, placed for a definite time in a weak field  $H$ , and then returned to  $H_0$ . The order of magnitude of  $T_1$  in the field  $H$  can be judged from the observed drop in the NMR signal. The measurement results were:

H, G	170	250	430	800
$T_1$ , sec	10	15	30	130

This raises the question of the spin-lattice relaxation mechanism that leads to so strong a dependence on the magnetic field.

It is well known [5] that spin-lattice relaxation in dielectrics can be satisfactorily explained only by assuming the presence of a noticeable concentration of paramagnetic impurities in the sample. But this does not lead to a strong  $T_1(H)$  dependence. It is natural to assume that in molecular crystals, of which naphthalene is a typical example, the spin-lattice relaxation is due to the interaction of the spin system with some solid-state excitations. In the temperature interval from 0 to  $300^\circ\text{K}$  it is reasonable, in the case of a molecular crystal, to consider phonons only, the decisive role being played by optical phonons, since the acoustical ones make a negligibly small contribution to the spin-lattice relaxation [5]. Only two-phonon processes, involving emission of one phonon and absorption of another, need be

considered.

Such processes can result in the transfer of an energy  $\lesssim \Delta$  ( $\Delta$  = width of band) to the phonon system. This mechanism should therefore be effective in weak fields ( $\mu H \lesssim \Delta$ , where  $\mu$  is the nuclear magnetic moment) and should vanish in strong fields ( $\mu H \gg \Delta$ ). To explain the behavior of the  $T_1(H)$  curve it must therefore be assumed that the width of the corresponding energy band is  $\sim 10^{-21}$  erg.

Furthermore, with such a spin-lattice relaxation mechanism, the time  $T_1$  in weak fields should depend exponentially on the temperature.

Indeed, a naphthalene sample cooled to  $77^\circ\text{K}$  can be taken out of a field  $H_0$  for a time of the order of one minute without a noticeable drop in the signal amplitude. Pound's experiment is successful also when the sample is cooled to the temperature of solid carbon dioxide. Removal of the sample from the working gap for 2.5 seconds did not change the signal noticeably. The signal dropped markedly when the sample was moved out into the earth's field for a time on the order of one minute.

From this we can establish the position of the energy band, by assuming that  $1/T_1 \sim \exp(-E/kT)$ . According to our estimates this level corresponds to a frequency  $\approx 10^3 \text{ cm}^{-1}$ , which falls in the region of the vibrational frequencies of the isolated molecules of the naphthalene.

Let us estimate the probability of the two-phonon process in the case of optical phonons. This can be done in the manner used for the case of acoustical phonons in [5], except that the series expansion of the spin-spin interaction energy should be not in terms of the deformation tensor but in terms of the displacements of the nuclei from the equilibrium position. We have

$$P_2 \approx \frac{162 \pi \hbar^3 F_0^2}{m^2 \omega_0^2 r^4} \frac{n}{\Delta} \varphi(\epsilon). \quad (2)$$

Here  $F_0$  is the energy of the spin-spin interaction in  $\text{sec}^{-1}$ ,  $m$  the proton mass in grams,  $\omega_0$  the position of the band above the ground state in  $\text{cm}$ ,  $\Delta$  the width of the band in ergs,  $n = \exp(-\hbar\omega_0/kT)$ ,  $\varphi(\epsilon)$  is a function of the order of unity when  $|\epsilon| \lesssim \Delta$  which tends rapidly to zero outside this interval, and  $\epsilon$  is the energy transferred to the spin system in a single scattering event.

Substituting here  $F_0 = 9.1 \times 10^4 \text{ sec}^{-1}$ ,  $\hbar = 10^{-27} \text{ erg-sec}$ ,  $m = 1.7 \times 10^{-24} \text{ g}$ ,  $\omega_0 = 1.7 \times 10^{14} \text{ sec}^{-1}$ ,  $r = 2 \times 10^{-8} \text{ cm}$ , and  $T = 300^\circ\text{K}$ , we obtain

$$P_2 \approx \frac{2 \cdot 10^{-21}}{\Delta} \varphi(\epsilon). \quad (3)$$

We have stated above that the experimental  $T_1(H)$  dependence requires the assumption that  $\Delta \approx 10^{-21}$  erg. Substituting this value in (3) and recognizing that  $\varphi(\epsilon) \sim 1$ , we get  $T_1 = 0.5 \text{ sec}$ . Agreement with experiment must be regarded as perfectly satisfactory if account is taken of the crude nature of the estimates.

Thus, a noticeable contribution to the transition probability can be made only by very

narrow energy bands.

It can be assumed that the existence of such bands is not a unique feature of naphthalene. Thus, for example for substituted naphthalenes and benzenes, for coronene, etc., the relaxation time in the field  $H_0$  is  $T_1 \sim 1$  min. It must be emphasized that the majority of the investigated substances did not contain noticeable concentrations of paramagnetic impurities. It is thus not excluded that the proposed mechanism plays a decisive role in the process of the spin-lattice relaxation in molecular crystals.

We are inclined to believe that the corresponding bands are brought about by deformation-induced intramolecular vibrations.

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#### INFRARED ABSORPTION IN CONDUCTING RUTILE CRYSTALS

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The question of the possible role of polarons in the conductivity of ionic crystals has been under discussion in the literature for a long time [1,2]. However, the difficulties arising in the investigation of transport phenomena in crystals with low carrier mobility, and ambiguities in the treatment of experimental results, lead to contradictions between conclusions drawn by different researchers, even those studying the same material. Such a situation developed, for example, during the course of an investigation of NiO [3].

A promising method of checking on the existence of polaron conductivity in the crystals is the study of the spectrum of the optic absorption by the carriers.\* The investigations reported here were made on single crystals of rutile ( $TiO_2$ ), chosen because it has been shown that the aggregate of its electric properties is undisputedly described within the framework of the theory of small-radius polarons, whereas the use of the usual "band" concepts leads to considerable difficulties [4].

The simplest method of introducing donors into rutile and creating an appreciable conductivity is to reduce it partially by annealing in vacuum or in a hydrogen atmosphere. With this, as noted in a number of papers [5-10], a broad band centered near  $6000\text{ cm}^{-1}$  appears in the absorption spectrum. The origin of this band was ascribed to absorption by various kinds of defects produced under such a heat treatment [6,7,9,10]. However, as shown by our experi-