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PHYSICS

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CHEMICAL SHIFTS OF FLUORINE NUCLEAR MAGNETIC RESONANCE SIGNALS IN IONIC CRYSTALS

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At present, the measurement of chemical shifts of nuclear magnetic resonance (n.m.r.) lines has found broad application in various fields of molecular physics and in the practice of chemical analysis. However, there are still very few works on the measurement of chemical shifts in the solid phase of a substance, although such measurements are of interest for the study of the electronic structure of a solid and for a number of other questions. The difficulty of measurements of this kind lies in the fact that the width of an n.m.r. line in solids usually exceeds the magnitude of the chemical shift by tens of times; nevertheless it can be observed experimentally, although with greater error than in liquids.

Chemical shifts in solids were first detected by Gutowsky and McGarvey (ˆ1) on rubidium and cesium nuclei in their halide compounds. Later several works were carried out on the nuclei of various halides and alkali metals with large quadrupole moments in ionic crystals ([2-6]). The main purpose of most of these works was to clarify the nature of the nuclear quadrupole coupling in the indicated substances. In the present work similar measurements are extended to Fˆ19 nuclei in fluorides whose metals are in the first and second groups of the Mendeleev table. From our point of view, such measurements are of interest not only for studying the electronic structure of solids, but also for elucidating the question of the position of the resonance of the free ion Fˆ−, as well as the influence of the surrounding medium on this ion. This question is of essential significance for the theory of chemical shifts in fluorine n.m.r. (ˆ7).

In the present work a radio-frequency spectrometer with output to a self-recording device, recording the derivative of the n.m.r. line, was used. The electromagnet was powered by an acid storage battery with a capacity of 288 ampere-hours. At a field level of 3700 gauss and after 5 hours of warming of the magnet, the field drifts uniformly at a rate of 2-3 gauss/hour, depending on the battery regime; the short-term instability of the field does not exceed

$1 \cdot 10^{-5}$. The radio-frequency generator is a circuit of Gutowsky et al. (^8) with a certain modification consisting in the separation of generation and detection on different halves of the 6N3P tube. Slow passage through the resonance region in frequency is provided by an additional capacitor, which is rotated by a motor.

The chemical shift

$$\xi = -\frac{\nu - \nu_e}{\nu}$$

(ν and ν_e are the resonance frequencies of the investigated and reference samples) is determined by the distance between the centers of the two lines. To avoid distortion of the center of the weak solid-state line by the intense line of the liquid reference when they are recorded simultaneously, small amplitudes of modulation of the magnetic field were used, so that the reference line occupied no more than 1/4 of the peak-to-peak width of the solid-state line (for example, for LiF, which has a peak-to-peak width of about 12 gauss, the doubled ampli-

modulation amplitude was 1.8 gauss). In addition, as a check in the case of narrower lines, the investigated substance and the reference were also placed in two different radio-frequency coils. In this case, at the location of the reference sample an additional, carefully measured field of the order of several gauss was produced, so that the reference line lay outside the central region of the line under study. Each measurement was made by passing twice through the resonance region (with and against the field drift), which makes it possible to eliminate the influence not only of field drift but also of distortion of the centers of both lines due to the time constant of the phase detector. The results were averaged over 4-8 such measurements. KF in aqueous solution served as the reference.

Fig. 1. Chemical shifts of fluorine lines (relative to F_2) in ionic crystals with metals of the first group (a) and second group (b) of the periodic system. The horizontal segments indicate the possible measurement error.

Figure 1 shows the results of the measurements. The origin of the chemical-shift scale has been referred to molecular fluorine (ξ for KF in aqueous solution relative to F_2 is equal to $5.48 \cdot 10^{-4}$). The vertical dashed line indicates the position of the reference resonance.

It should be noted that the signals for KF and RbF are distorted by saturation because of long relaxation times; consequently, the determination of ξ for them is less accurate.

The measurement results show that the chemical shifts of the fluorine NMR line, and hence the magnetic shielding, decrease as the atomic number of the metal increases (with the exception of LiF). This regularity is opposite to that observed for binary covalent fluorine compounds in the liquid phase (9). This apparently indicates the specific character of the influence of the solid-state

structure on the nuclear magnetic shielding of fluorine. It also follows from the results obtained that the fluorine ion in crystals differs substantially from the free ion.

On the basis of existing theories of chemical shifts in ionic crystals, the following factors affecting the magnetic shielding of fluorine may be indicated:

a) partial covalency of the bond; the detailed theory of Iosida and Moria (10) shows that ξ should decrease with increasing degree of covalency;

b) overlap of the electronic charges of neighboring ions; Kondo and Yamashita (11) gave a theoretical formula which shows a decrease of shielding with increasing degree of overlap, expressed through the overlap integral.

In our case factor a) cannot play an essential role. Otherwise the regularity would be the reverse, since it is known that the covalency of the bond in fluorides is greater the greater the electronegativity of the metal atom (i.e., the smaller its atomic number). However, this factor probably explains the anomalous position of the signal in the LiF crystal, which has a comparatively large degree of covalency.

Factor b) may play the predominant role. Since, however, at present we do not have specific data on the overlap integrals in the crystals investigated, it is difficult to draw more definite conclusions.

In the theoretical calculations mentioned above, which are based on

within Ramsey' s general theory ([12]), believe that the change in the magnetic shielding of the nucleus occurs only at the expense of second-order paramagnetism. For the fluorine atom, owing to the small number of inner electrons, a partial change of the diamagnetic term in different compounds apparently cannot be excluded. In addition, the electric fields in crystals also affect the magnetic shielding. The theory of Marshall and Pople ([13]), for the case of proton resonance in liquids, shows that the application of a homogeneous electric field decreases the shielding of the nucleus. One may suppose that crystal fields exert an analogous effect. However, in comparison with the regularity observed experimentally, this effect has the opposite sign, since the influence of crystal fields decreases with increasing internuclear distance.

At present, analysis of the results obtained is continuing; in particular, it is planned to make a theoretical estimate of the degree of overlap of the electron shells for crystals of the first group.*

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* The overlap of electron charges was considered by Löwdin ([14], [15]) in calculating the binding energy in ionic crystals. For some substances he also carried out calculations of overlap integrals, but his works contain no calculations for the substances of interest to us.

Note: Figure translations are in progress. See original paper for figures.