NQR ^{127}I Spectroscopy of Layered Inorganic Compounds Intercalated with Aromatic Amines*

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NQR spectroscopy was used to study the intercalating influence on the iodine electric field gradient of lead(II) and cadmium(II) iodides. We used pyridine, piperidine, aniline and quinoline, as guest substances. In the intercalates the NQR frequencies and their dependence on temperature in different crystalline phases were studied. The peculiarities of chemical bonds and crystal structures were discussed.

Introduction

Intercalates are inclusion substances with layered structure. The intercalation is possible in highly anisotropic compounds where intralayer interactions are much stronger than interlayer ones. The "guest" compounds are included in the Van der Waals splits between the layers. The intercalates differ from usual doped blends in that the "guest" molecules are only in the interlayer space. Graphite, dichalcogenides of transition metals, transition metal halides with layered structure, and rare earth oxyhalides can serve as examples of hosts of intercalates.

The intercalation of organic molecules was first observed in compounds of the second and the third kind (in the layered halcogenides and halides) [1, 2].

We tried to get data on the structure of intercalates that are derivatives of semiconducting layered PbI_2 and CdI_2. They have a sandwich-like crystalline structure with "sandwiches" made of a layer of metal cations (M^{2+}) contained between two layers of iodide anions (I^-). Metal atoms are co-ordinated by six iodine atoms. Every iodine forms bonds with three neighbouring metals cations, these bonded atoms forming stable layers (Figure 1). Two different crystalline structures can be formed, depending on the relative location of halogen atom planes having octahedral (space group P6mc) or rhombic (space group P3m1) symmetry around the metal. In the rhombic symmetry, the lattice parameter "c" of PbI_2 is up to 3 times larger, and of CdI_2 is up to 2 times larger, than in the first symmetry. Therefore the electric field gradient (efg) on the iodine nuclei in PbI_2 is different for the rhombic phase (eQq=30 MHz) and the octahedral phase (eQq=115 MHz). NQR ^{127}I data on CdI_2 are known only for the octahedral phase (eQq=98.3 MHz) [3].

Organic molecules may fill interlayer spaces in these compounds. PbI_2 and CdI_2 could be intercalated by donor molecules, so we used for intercalation nitrogen-containing aniline, pyridine, piperidine, quinoline. In this case, unpaired nitrogen electrons are interacting with electronegative halogen atoms. It is possible that intercalation depends on an intercalant – intercalant interaction also. The interlayer distance ("c" parameter of the lattice) is increased in accordance with the size of the intercalants that accommodate orderly between the matrix layers, the period of the accommodation being a small multiple of "a". Thus a flat superlattice is formed in $Pb(Cd)I_2$. The intercalant molecules can be placed in the Van der Waals splits of the lattice in small piles parallel or perpendicular to the layers of the host crystal (Fig. 1 B a–c). Multiples of the period and the number of molecules in the layer or in the pile are determined by the intercalate stoichiometry.

The same model allows to describe specific three-dimensional effects of ordering, such as the stages of the intercalation when the filled splits alternate with unfilled ones with periods of 2, 4, 6 layers.

Depending on the conditions of the synthesis one gets different phases. Besides, in the course of storage some "superfluous" intercalant molecules could evaporate. Influence of the synthesis conditions on the structure and the degree of ordering in two- and three-dimensional intercalate structures were discussed in [4].

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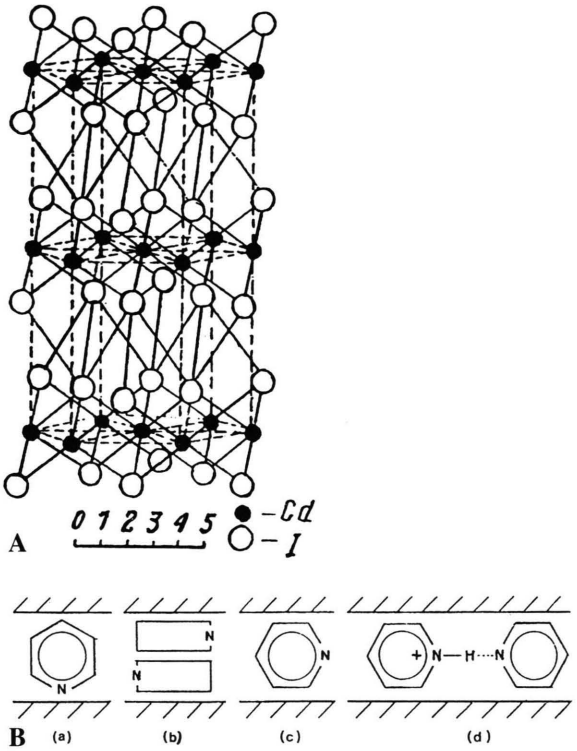

Fig. 1. A) Hexagonal structure of cadmium(II) iodide. B) The possible locations of the pyridine rings in intercalates $(Py)_{1/2}MX_2$: a, b) heterocyclic locations; c) a location with the nitrogen unpaired electrons perpendicular to X-M-X layers; d) H-bond between pyridine molecules.

NQR was repeatedly used in studies of the intercalate structures [5–9]. Relevant work was published by Lyfar' and Ryabchenko [8, 9]. Temperature dependences of the ^{127}I NQR frequencies and spin-lattice relaxation T_1 in the PbI_2 intercalates with aniline and piperidine were presented there. It was shown that intercalation results in a marked decrease of the two-dimensional features in the spin-phonon interaction (especially in the piperidine intercalate), though the temperature dependences of frequencies and T_1 are not typical for three-dimensional crystals.

Results and Discussion

We carried out detailed studies of the temperature dependence of the NQR frequencies and of phase transitions with the changing of the superlattice period.

The composition of the compounds investigated was the following: PbI_2+aniline, PbI_2+2 pyridine, PbI_2+piperidine; CdI_2+3 aniline, CdI_2+2 piperidine, CdI_2+quinoline.

PbI_2 Intercalates

In earlier [10, 11] studies of the aniline intercalate of PbI_2 by powder X-ray analysis, two phase transitions were observed at 145 and 223 K. By infra-red spectroscopy data the last of these two transitions was attributed to the reorientation of hydrogen bonds N–H ... N in the layers of the organic intercalant (Fig. 1 B d).

In our NQR studies of the same intercalate we found out that: 1) two (35.08 and 39.85 MHz) or four lines discovered early [9] and assigned to different sites of PbI_2 molecules vanish with storage time; 2) at 230 K there is a break in the temperature dependence of the frequency for the second site of lead iodide (see, Figure 2). These

Table 1. The ^{127}I NQR frequencies at 77 K in different crystalline phases of aniline, piperidine and pyridine intercalates of lead(II) iodide.

Intercalant	Phase	NQR frequencies		eQq	η
		MHz	MHz	MHz	
		$\Delta m = 1/2-3/2$	$\Delta m = 3/2-5/2$		
Aniline	1	35.08	39.85	146.9	85
	2	71.56	105.74	371.0	55
Piperidine	1	17.1	20.21	72.3	80
	2	82.34	109.00	390.7	67
Pyridine	1	76.3	92.1	335.45	78
	2	75.3	80.9	302.7	91

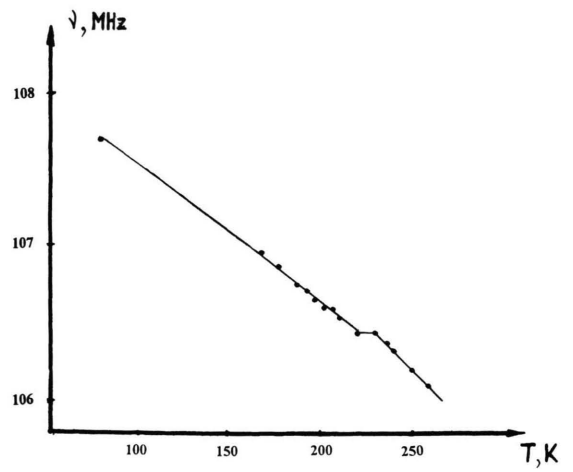

Fig. 2. Temperature dependence of the ^{127}I NQR frequency (transition $\Delta m = 3/2-5/2$) in aniline intercalate of lead(II) iodide.

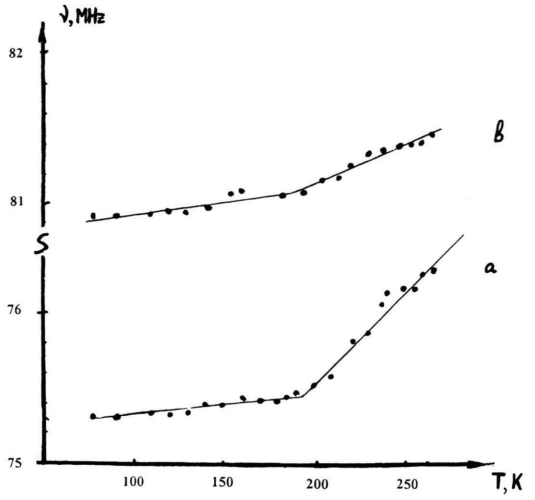

Fig. 3. Temperature dependences of the ^{127}I NQR frequencies ($\Delta m = 1/2-3/2$ (a) and $\Delta m = 3/2-5/2$ (b)) in pyridine intercalate of lead(II) iodide.

data suggest the existence of several phases with different stages and with phase transitions due to the disappearance of old intercalate or to the birth of new phases.

The NQR frequencies of matrix molecules for intercalate phases with different stages differ substantially. Examples are shown in Table 1. Besides the frequencies for PbI_2+aniline, in one of the phases of intercalate PbI_2+piperidine the frequencies were found to be 17 and 20 MHz [9], and in the other 82.34 and 109.0 MHz (our measurements). In the pyridine intercalate of PbI_2 the lines of two phases are of different intensity. However we want to note that the different phases of intercalates could be due to the different symmetry of matrix molecule packing in the layers. The changes of the NQR frequencies at phase transitions in the organic phase are much smaller (Figure 2).

We found for the second phase of the pyridine intercalate of PbI_2 a positive temperature coefficient of the NQR frequencies (Figure 3). One can distinguish two ranges with different values of $d\nu/dT$: in the low temperature range $d\nu/dT = 1.06$ kHz/grad for the lines of both transitions $\Delta m = 1/2-3/2$ and $\Delta m = 3/2-5/2$; in the high temperature range (>200 K) $d\nu/dT = 10.9$ kHz/grad for line $\Delta m = 1/2-3/2$ and $d\nu/dT = 4.75$ kHz/grad for line $\Delta m = 3/2-5/2$.

It is possible that the unusual positive sign of $d\nu/dT$ is due to a decrease of charge transfer to the iodine atoms and simultaneously to an increase of the contribution of the interaction of pyridine molecules with each other (Figure 1B d).

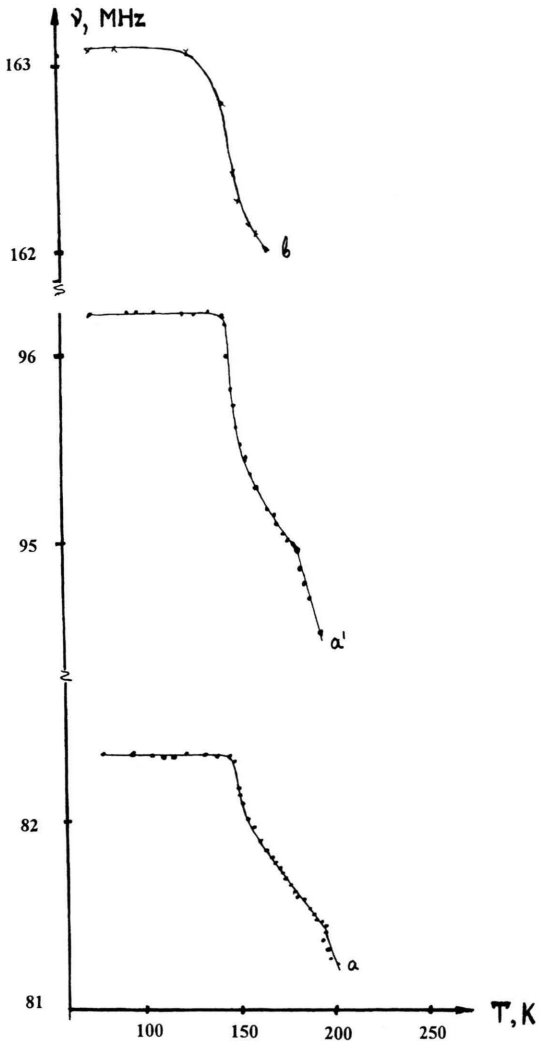

Fig. 4. Temperature dependences of the ^{127}I NQR frequencies ($\Delta m = 1/2-3/2$ (a, a′) and $\Delta m = 3/2-5/2$ (b)) in piperidine intercalate of cadmium(II) iodide.

CdI_2 Intercalates

It was mentioned earlier that the lattice parameters "*c*" of the unit cell of the phase with octahedral symmetry for CdI_2 is smaller than for PbI_2. It is possible that the more compact structure of the cadmium iodide matrix results in a more rigid structure of the cadmium iodide intercalates.

Besides, the different atomic masses of the cadmium and lead ions also must influence the different features of the intercalates based on cadmium and lead iodides. Particularly the phonon frequencies in CdI_2 will increase

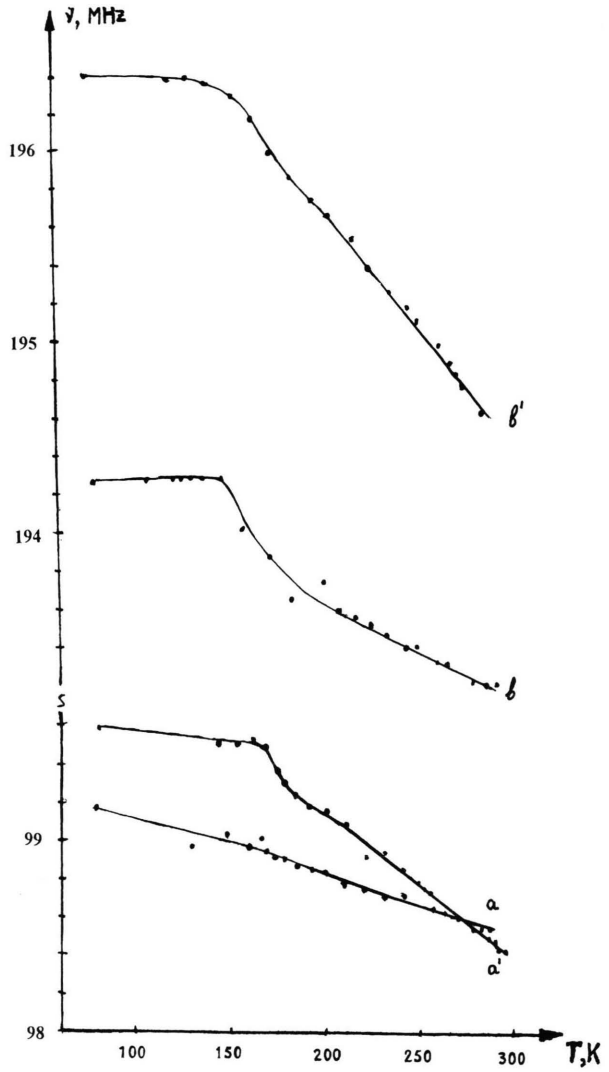

Fig. 5. Temperature dependences of the ^{127}I NQR frequencies ($\Delta m = 1/2-3/2$ (a, a′) and $\Delta m = 3/2-5/2$ (b, b′)) in quinoline intercalate of cadmium(II) iodide.

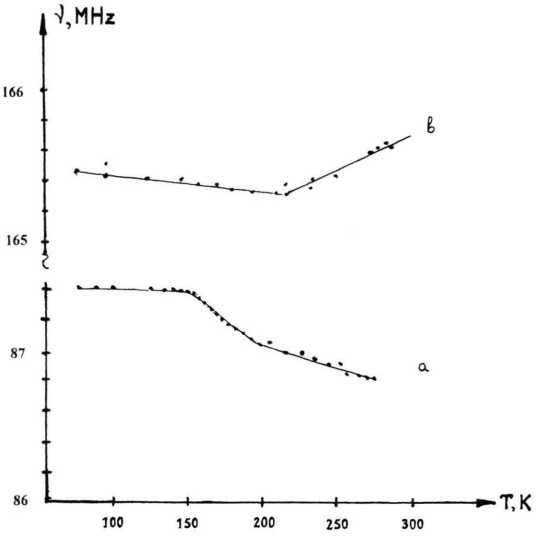

Fig. 6. Temperature dependences of the ^{127}I NQR frequencies ($\Delta m = 1/2-3/2$ (a) and $\Delta m = 3/2-5/2$ (b)) in aniline intercalate of cadmium(II) iodide.

with respect to those of PbI_2 proportionally to the square root of the reversed relation of the effective masses participating in the vibrations (about 1.2). Consequently the characteristic Debye temperature must increase also. If for lead iodide Θ_D (Debye temperature) is about 150 K, for cadmium iodide it must be 180–190 K.

Therefore it is not surprising that the temperature dependence of the NQR frequencies in the cadmium iodide intercalates with aniline, piperidine and quinoline have pronounced peculiarities (Figures 4–6). The NQR frequencies change very little if the temperature is lower than Θ_D. At higher temperature abrupt changes are observed, leading to a linear decrease of the NQR frequencies with temperature. The values of $d\nu/dT$ are different for different intercalates but they are larger than $d\nu/dT$ for initial CdI_2.

The NQR frequencies in the case of pure CdI_2 grow when the temperature increases in the region 5–50 K and don't change on further heating [9]. Though the parameter "c" increases at intercalation, rigid packing of the layers in cadmium iodide is preserved. So the averaging of the efg on the iodine nuclei due to the lattice vibrations happens at higher temperatures than in lead iodide intercalates.

Conclusion

In conclusion let us note that compacting of the molecular packing in the cadmium iodide intercalates can result in significant shortening of the distance N . . . I, and then in an increase of the electron transport to the point where usual molecular complexes are formed. However the layer packing is kept in these complexes. We observed the NQR signals of these complexes but there are other peculiarities as well [12].

Thus the NQR method 1) unambiguously demonstrates the difference of the structure and intracrystalline electric fields in phases with different stages; 2) gives the opportunity to study phase transitions that take place in the organic part of the intercalates; 3) shows possible per-

culiarities of the behaviour of the intercalate phonon spectra of different matrixes with analogous structure.

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