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#### EFFECT OF LATTICE-DISTORTING IMPURITIES ON PROTON MAGNETIC RESONANCE SPECTRA

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It was observed in proton magnetic resonance (PMR) investigations of laboratory-synthesized potassium hexacyanoosmiate  $K_4Os(CN)_6 \cdot 3H_2O$  that the spectra of polycrystalline samples registered at room temperature (Fig. 1), differ greatly from the spectra of the previously investigated isomorphous potassium ferrocyanide  $K_4Fe(CN)_6 \cdot 3H_2O$ . A study of the central peak in the spectrum has shown that its width does not exceed several hundredths of an Oersted and can therefore be attributed only to the diffusion of the water molecule in the crystal lattice. (The large width of the central maximum on Fig. 1 is due to the large modulation used here to register the weak "wings" of the spectrum.) This diffusion could presumably be due to the presence of free or weakly bound water adsorbed by the sample, but thorough drying of the samples did not change the form of the spectra.

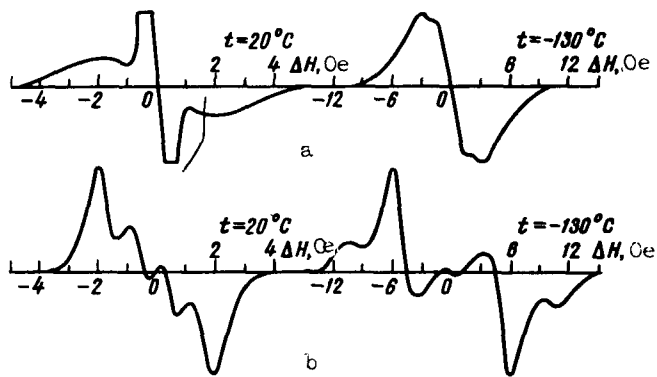


Fig. 1. PMR spectra (derivatives of absorption lines) of polycrystalline  $K_4Os(CN)_6 \cdot 3H_2O$  at different temperatures as indicated in the figure; a - before purification, b - after purification.

Cooling the samples to "freeze" the water-molecule mobility changed the intensity of the narrow central peak little, down to  $\sim -59^\circ C$ , where the peak vanished within a temperature interval of several degrees. But even below this temperature, a noticeable central maximum remained in the spectra and the spectrum, as seen from Fig. 1, differs appreciably from the characteristic spectra of hydrates with "rigid lattice" (see [1]) even at  $-130^\circ C$ . The temperature variation of the second moments ( $S_2$ ) also offers evidence that the mobility of the water

molecules decreases very little with decreasing temperature (Fig. 2, curve a), and at  $-130^{\circ}\text{C}$  the value of  $S_2$  is much lower than the values characterizing the water molecule in the "rigid lattice."

A suggestion was made that this high water-molecule mobility is due to impurities distorting the crystal lattice. Analysis of the samples has shown that they can contain several per cent of impurities, principally KCN. We have therefore recorded FMR spectra of  $\text{K}_4\text{Os}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  and of the isomorphous compounds  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_4\text{Ru}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  at different impurity contents. The samples were purified by multiple (up to five- and sixfold) recrystallization. After several recrystallization cycles, the usually yellow potassium ferrocyanide acquired a bright color with yellow hue, and the potassium hexocyanosmiate became white with light bluish hue.

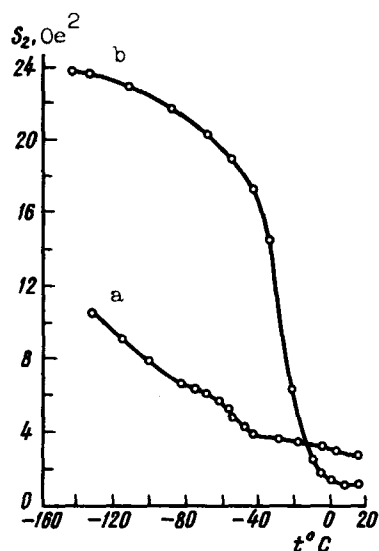


Fig. 2. Temperature dependence of second moments of  $\text{K}_4\text{Os}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ; a - before purification, b - after fivefold recrystallization.

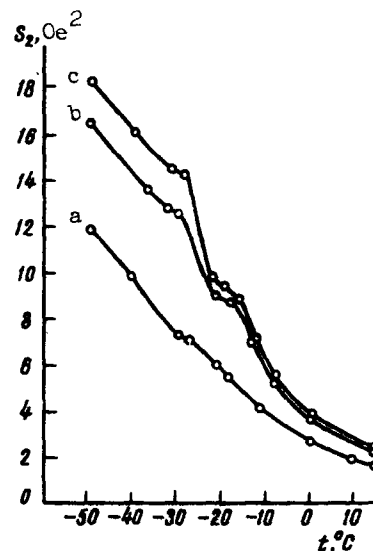


Fig. 3. Temperature dependence of second moments of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ; a - chemically pure sample, b - after twofold recrystallization, c - after fivefold recrystallization.

After purification of the samples, the form of the spectrum and the temperature dependence of the second moments changed appreciably, as seen from Figs. 1 and 2. We note that the spectra of all three investigated compounds acquire a common form, similar to that shown in Fig. 1b, after thorough purification. At low temperature, the spectra of all three compounds are similar to that shown in Fig. 1b for the corresponding temperature.

Figure 3 shows the temperature dependence of  $S_2$  for commercial (chemically pure) and purified (by twofold and fivefold recrystallization) potassium ferrocyanide. We see that as the samples become purer the temperature interval in which  $S_2$  changes becomes much narrower, and the jump of the second moment at the point of the ferroelectric phase transition ( $-24.5^{\circ}\text{C}$ ) becomes more and more pronounced. It should be noted in this connection that the difference in the form of the spectra and in the character of the temperature dependences of the second

moments, reported in [2-4] for polycrystalline potassium ferrocyanide, are apparently connected with precisely the presence of small amounts of impurities in the investigated samples.

The influence of impurities on the NMR nuclei with spin  $I > 1/2$  and with quadrupole moment is well known [5,6] and is due to the fact that the impurity atoms, vacancies, and other lattice defects produce different electric-field gradients at the places where the resonating nuclei are localized, and also to the decrease in the relaxation time, owing to the large diffusion rate in a crystal with defects.

This is the first observation of the described strong influence of relatively small impurity contents on proton magnetic resonance spectra. This phenomenon is apparently caused by the well known increase of the diffusion mobility (in this case, of the  $H_2O$  molecules) in a crystal with defects.

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#### LASER WITH NEODYMIUM-ACTIVATED $\alpha$ -GAGARINITE

(Devoted to Man's First Flight in Space)

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Gagarinite is a natural fluoride of rare earths ( $TR^{3+}$ ), sodium, and calcium, with idealized formula  $NaCaYF_6$ . This mineral was discovered in the USSR in 1958 [1] and named in honor of the first astronaut in the world Yu. A. Gagarin.

In this communication we present preliminary results of investigations of a new laser based on an  $\alpha$ -gagarinite crystal activated with  $Nd^{3+}$  and operating at 300°K.

We used  $\alpha$ -gagarinite crystals grown by the Stockbarger method in an HF atmosphere [2]. As is well known, gagarinite has two polymorphic modifications, the high-temperature one having a fluorite-type structure. In a definite region of the  $NaF-CaF_2-YF_3$  system, the cubic modification ( $\alpha$ ) is retained in a wide temperature interval. It is this  $\alpha$  modification which we investigated.

The samples for the study of the stimulated emission were prepared from synthetic single crystals of satisfactory optical quality in the form of cylindrical rods ~30 mm long and ~6 mm in diameter, with plane-parallel (~15") end faces. The activating-impurity con-