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Experimental Proof of the Existence of Water Clusters in Fullerene-Like PrF_3 Nanoparticles

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Synthesized fullerene-like nanoparticles of the Van Vleck paramagnet PrF_3 have been studied by nuclear magnetic resonance cryoporometry. Water clusters have been discovered in the internal cavities of the nanoparticles. The analysis of the experimental data indicates that the cluster radius is 1–2.3 nm. The obtained data agree well with the high-resolution transmission electron microscopy data.

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Recently, the interest in nanoparticles has been steadily increasing owing to their unique physical and chemical properties. Deposition from colloid solutions is a well-elaborated method, which makes it possible to obtain nanosize samples of double and triple rare-earth fluorides [1]. A modification of this technology with the use of microwave radiation is described in [2], where it was shown that there are internal cavities in the synthesized particles (such nanoparticles are called fullerene-like nanoparticles). This technology was used to synthesize a series of crystalline fullerene-like PrF_3 nanoparticles [3–5]. Since the hydrothermal synthesis is performed in an aqueous solution, it is possible to suppose that water is located in the internal cavities of such nanoparticles. The aim of this work is to test this hypothesis using nuclear magnetic resonance cryoporometry and high-resolution transmission electron microscopy methods.

Studies using an HR TEM JEM-2100 F/SP high-resolution transmission electron microscope with a resolution of 0.14 nm and an input voltage of V_a = 200 kV were performed at the RIKEN Institute, Wako, Saitama (Japan). Figure 1 shows images of the PrF_3 nanopowders (subjected to microwave radiation) taken with this microscope. One can see the presence of internal cavities in the fullerene-like PrF_3 nanoparticles. A single particle may have one or several cavities (Fig. 1a); the size distribution of the cavities is also observed. The enhanced view of the nanoparticles is shown in Fig. 1b. It can be seen that the cavity radius is about 3 nm. Figure 1c shows an image of a nanoparticle of the PrF_3 sample precooled to the liquid nitrogen temperature. It can be seen that the nanoparticle structure is destroyed. Such destruction can be explained by the presence of water inside the cavities, which has an anomalous thermal expansion coefficient and expands during freezing. No destroyed particles were found in the samples that were not subjected to cooling.

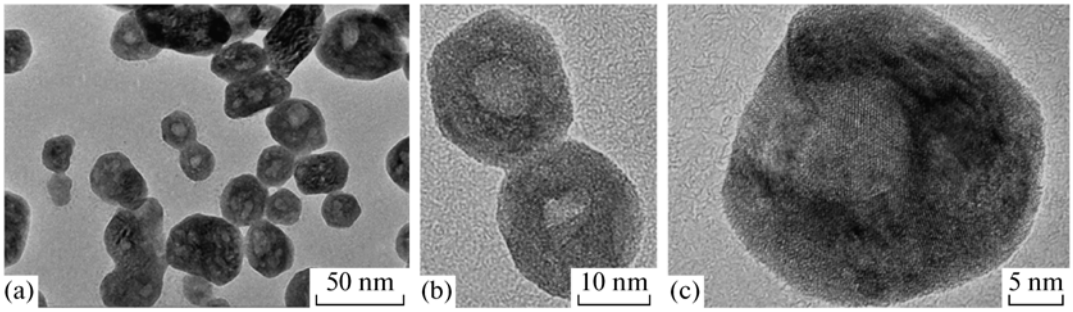

Fig. 1. High-resolution transmission electron microscope image of the PrF_3 nanopowder.

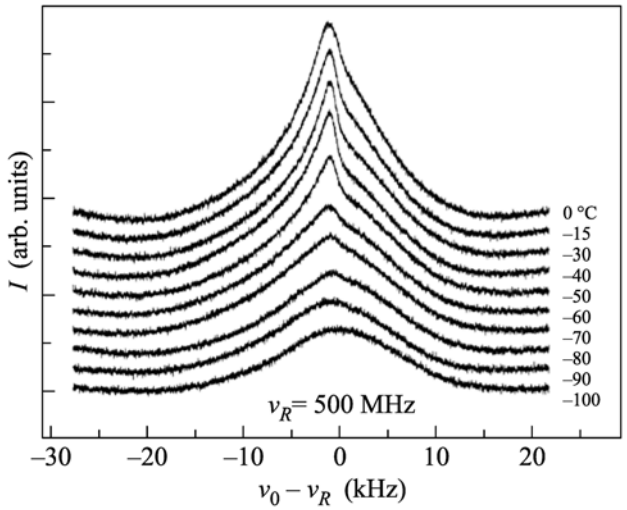

Fig. 2. Temperature dependence of the ^{1}H nuclear magnetic resonance spectra of the PrF_3 nanopowder; H_R = 117440 Oe.

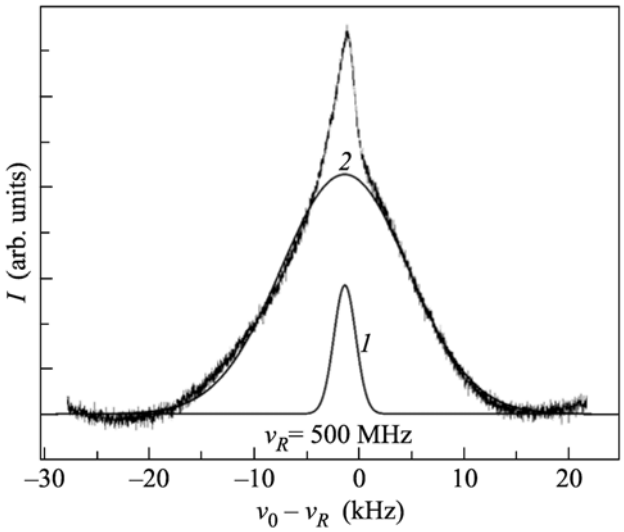

Fig. 3. Approximation of the ^{1}H nuclear magnetic resonance spectrum of the PrF_3 nanopowder at $T = -40$°C by two Gaussian lines.

Nuclear magnetic resonance cryoporometry can be applied to the measurement of the pore sizes and the construction of the pore distribution from 1 to 100 nm. It is well known that the physical properties of a liquid confined in small pores can strongly differ from the properties of the bulk liquid [6]. A liquid that fills the free space of a porous medium always has a relatively large number of surface atoms. One of the relevant consequences is the decrease in the melting temperature. This effect is the basis of the cryoporometry method for studying the structural parameters of porous media, which uses the relation between the melting temperature of the liquid introduced into the pores and the pore size. It is convenient to determine the fractions of the solid and liquid phases of this substance from pulsed nuclear magnetic resonance data, since the solid phase has the shorter spin–spin relaxation time T_2 than the liquid phase.

The decrease in the phase transition temperature can be described by the Gibbs–Thompson equation [6, 7]

$$\Delta T = T_0 - T(R) = \frac{4\sigma T_0}{\Delta H \rho} \frac{1}{R}, \quad (1)$$

where σ is the surface energy at the liquid/solid interface, T_0 is the normal melting temperature, $T(R)$ is the melting temperature of the crystal with the radius R, ΔH is the melting enthalpy, and ρ is the crystal density.

The experimental studies have shown that, when using this equation, it is necessary to take into account that there is a nonfreezing layer d of 1–5 Å between the pore surface and crystal down to limiting low temperatures. A modified equation looks as follows:

$$\Delta T = \frac{K}{R - d}. \quad (2)$$

To use a decrease in the melting temperature for measuring the pore sizes, a porous sample containing a liquid is cooled until all of the liquid freezes. As a rule, water (K = (573–582) kÅ, d = (3–5) Å) or cyclohexane (K = (1825–2001) kÅ, d = 7 Å) is chosen as the liquid [6].

To test the hypothesis of the presence of water in the cavities of the PrF_3 nanoparticles and perform cryoporometry, we recorded the ^{1}H (500 MHz) spectra on an AVANCE II-500 (Bruker) nuclear magnetic resonance spectrometer. The spectrometer functioned in the internal stabilization mode on the ^{2}H resonance line. We used 90-degree pulses when recording the ^{1}H nuclear magnetic resonance spectra. The pulse delay was 0.5 s. The number of scans was 256. Figure 2 shows the temperature dependence of the ^{1}H nuclear magnetic resonance spectra.

It can be seen in Fig. 3 that there are two lines in the nuclear magnetic resonance spectrum of protons, which can be attributed to the protons of water molecules. The presence of two lines can be explained by the fact water is present in the internal cavities of the PrF_3 nanoparticles (narrow line *1*) and as bound water (wide line *2*). It is obvious that the intensity of the narrow line is strongly temperature-dependent. Then, the nuclear magnetic resonance spectra were approximated by two Gaussian lines (Fig. 3). The approximation parameters (width, intensity) were obtained. As a result, the temperature dependence of the intensities

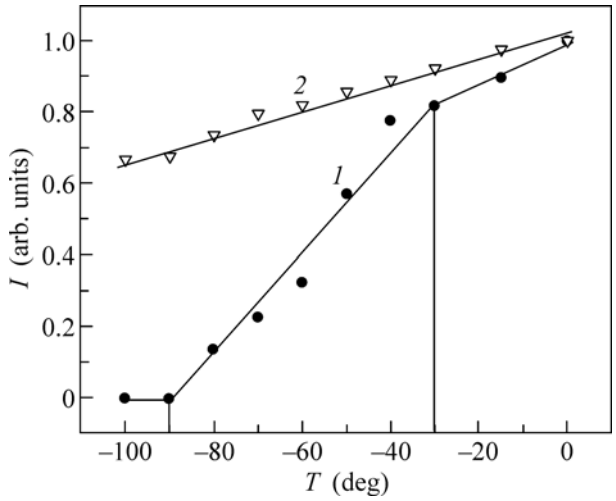

Fig. 4. Temperature dependence of the intensities of the two Gaussian lines in Fig. 3.

for both lines was plotted (Fig. 4). It can be seen in Fig. 4 that water freezes in the internal cavities of the PrF_3 nanoparticles in the temperature range from −30 to −90°C. This is related to the size distribution of cavities. The estimate by Eq. (2) gives the cavity radius $R = (1–2.3)$ nm, which agrees well with the high-resolution transmission electron microscopy data (Fig. 1). The temperature dependence of the intensity of the wide line (line *2* in Fig. 4) can be explained by the detuning of the nuclear magnetic resonance probe when the temperature is lowered, since the observation parameters of all spectra were deliberately kept constant.

The presence of the wide line in the spectrum indicates the enormous fraction of bound water, which poorly agrees with the size of the sample surface. Water molecules were probably captured inside the crystal lattice in the process of the instantaneous growth of nanoparticles during the chemical reaction. Owing to the subsequent microwave radiation treatment, water molecules apparently start to form clusters moving along the crystal lattice simultaneously with the reconstruction of the crystal lattice of nanoparticles. The particles become more single-crystal [3].

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