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Magnetic molecular clusters as promising materials for refrigeration in low-temperature regions

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Abstract
A wide class of magnetic molecular materials—molecular clusters with high magnetic moment containing 3d transition metals (such as 'Fe_8', 'Mn_{12}ac', etc)—have been considered from the point of view of their use as refrigerants in low-temperature regions. The consideration was made in the framework of the model based on the Langevin theory of a superparamagnet. The magnetic entropy change caused by a change in an external magnetic field was calculated for various magnetic clusters. The estimations made show that the magnetic molecular clusters could be promising materials for magnetic refrigeration in low-temperature regions (below about 20 K).

1. Introduction

Applications of cryocoolers capable of cooling in the temperature range of 1.8–20 K are quite diverse. They include, for example, hydrogen and helium liquefiers, superconducting magnets, SQUID devices, medical instrumentation and various scientific research applications. Superconducting magnets, which can produce high permanent magnetic fields, are widely used in medicine (in magnetic resonance imaging (MRI) systems) and in laboratories for scientific purposes. Usually they are cooled by liquid helium, since superconducting materials capable of holding strong magnetic fields have low temperatures of transition to the superconducting state. Especially effective is the magnet cooling by superfluid liquid helium with the temperature of 1.8 K. The use of liquid helium is not convenient, or profitable from the economic point of view, since the replenishment of liquid helium lost by evaporation is a difficult procedure and is accompanied by considerable loss of expensive liquid helium. Some MRI systems, in order to recondense evaporated helium, use Claude cycle helium liquefiers, which are quite complicated and expensive. Small and low-energy consumption cryogenic refrigerators are needed to make closed systems, providing permanent operation of superconducting magnets.

According to theoretical estimations and experimental investigations the use of the magnetocaloric effect (MCE) for cooling in the temperature range below 20 K is quite promising [1–4]. One of the main problems in creating an effective magnetic cryocooler is the search for an appropriate working material with a high magnetic entropy change, ΔS_M, under the change of magnetic field. In the temperature range below 20 K the Carnot thermodynamic cycle and paramagnetic materials are usually used. Certain success has been achieved using gadolinium gallium garnet $Gd_3Ga_5O_{12}$ (with a Neel temperature $T_N \sim 0.8$ K [5]) and dysprosium aluminium garnet $Dy_3Al_5O_{12}$ ($T_N \sim 2.54$ K [5]) in paramagnetic temperature ranges for $T < 20$ K [6, 7]. $Dy_3Ga_5O_{12}$ and $DyVO_4$ have also been studied as promising refrigerants for the mentioned temperature range [8, 9]. Kuz'min and Tishin [5] theoretically showed that rare earth orthoaluminates ($RAlO_3$) are more advantageous as refrigerants than the gadolinium and dysprosium garnets in the temperature range 4.2–20 K. Later their results were confirmed by Kimura *et al* [10].

In nanocomposite magnetic materials (materials containing nanosized magnetic particles) the enhancement of the MCE due to superparamagnetism should be observed as was discussed by a number of authors [11–15]. Experimentally, the

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