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The use of gadolinium-dysprosium rare-earth alloys as the working substance of refrigerators

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In the Soviet Union and in other countries experimental and development work is being carried out on magnetic refrigerators.

In order for a cooling device be sufficiently powerful it is necessary to obtain the largest possible change in the magnetic part of the entropy ΔS_M of the working substance when the external magnetic field is changed within the operating temperature range. It is well known that the maximum value of ΔS_M for ferromagnets is achieved in the neighborhood of the ferromagnetic–paramagnetic transition temperature. Consequently, the Curie point of the materials that comprise the working substance of a refrigerator operating at room temperature must lie in the range 273-293 K. Alloys of heavy rare-earth metals with Gd have these properties.[1-3]

The use of only pure Gd as the coolant is not effective, since the peak of the temperature dependence of $\Delta S_M(T)$ is in the temperature range below the Curie point of Gd. Therefore, for operation with Gd at room temperature, one must use only the left branch of this curve.

Among the more promising materials for use in magnetic refrigerators are Gd-Dy compounds.[2] It should be noted that in Dy the helicoidal antiferromagnetic–ferromagnetic phase transition is about 90 K below the temperature where the paramagnetic state is destroyed. As a result, Gd_xDy_{1-x} compounds can be used successfully as the cooling agent over a wide temperature range.[4] Another advantage of Dy is that the ion of this rare-earth metal has a large magnetic moment. The addition of a small amount of Dy atoms to Gd increases the total magnetic moment of the working substance and brings about a large increase in the efficiency of the refrigerator.

A purely practical advantage of Gd_xDy_{1-x} alloys is their relatively simple technology and low price as compared to other rare-earth metals. This circumstance is very important to the prospects of developing actual refrigeration devices based on the rare-earth metals.

The purpose of this investigation was to study the Gd_xDy_{1-x} compounds that have been proposed for the development of a composite working substance. To select the maximally efficient cooling agent the most important factor to study is the temperature dependence of the change in the magnetic part of the entropy, $\Delta S_M(T)$.

The simplest method of determining the jump ΔS_M is to calculate it from the known field and temperature dependences of the magnetization $I(T)$ of the material. The

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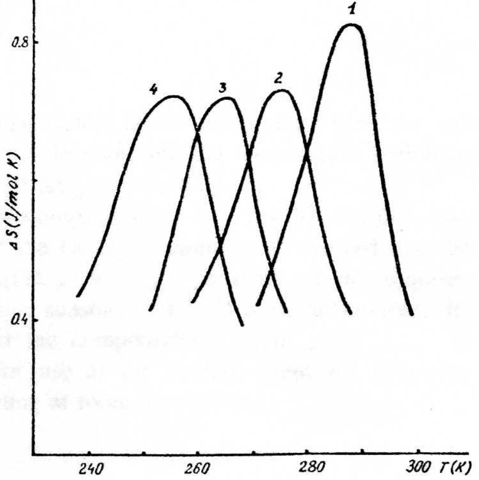

FIG. 1. Temperature dependences of the change in the magnetic part of the entropy, $\Delta S_M(T)$, in a magnetic field $B = 1.6$ T for Gd_xDy_{1-x} compounds: 1) Gd; 2) $Gd_{0.90}Dy_{0.10}$; 3) $Gd_{0.80}Dy_{0.20}$ 4) $Gd_{0.70}Dy_{0.30}$.

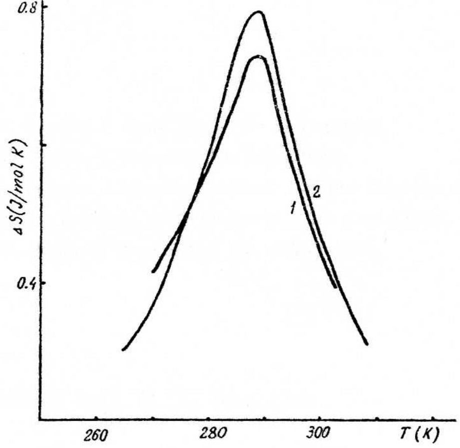

FIG. 2. Temperature dependences of the change in the magnetic part of the entropy, $\Delta S_M(T)$, in a magnetic field $B = 1.6$ T for a composite working substance $Gd_{0.59}(Gd_{0.90}Dy_{0.10})_{0.41}$. 1) Calculation; 2) experiment.

calculations are performed with the use of the formula

$$\Delta S_M = -\int_0^{B_{max}} \left(\partial I/\partial T\right)_B dB.$$

In this work we studied experimentally the dependence of the magnetization of Gd_xDy_{1-x} on T and B. The magnetic field was varied in the range up to 1.6 T and the temperature of the sample from 230 to 330 K. The magnetization was measured by the inductance method. The sample, in the shape of a rod of dimensions 1 × 1 × 4 mm, or a set of thinner plates were placed within the measuring coil, consisting of two windings connected in opposition. Subsequently and electromagnet of the armored type was developed. The samples were cut with a spark cutter and the damaged layer was removed. The method of preparation was similar to that described in Refs. 2 and 3. In these experiments we studied samples of Gd_xDy_{1-x} of the following composition: $x = 1$, 0.9, 0.8, and 0.7.

To determine the numerical values of the temperature derivative of the magnetization at constant magnetic field we used the curves of $I(T)$. The integration over the magnetic field was carried out with the use of a series of curves of the field dependence of the magnetization $I(B)$ at constant temperature.

The curves of $I(T)$ show a sharp falloff in the region of the phase transition, which is an indication of typical ferromagnetic behavior of the Gd_xDy_{1-x} alloys. An analysis of the data shows that in a constant magnetic field the variation of the magnetization as a function of the temperature $I(T)$ of the compounds with the higher dysprosium concentrations are located at the lower temperatures. It should be noted that each curve of $I(T)$ has an inflection point, where the second derivative $\partial^2 I/\partial T^2 = 0$. This point corresponds to the maximum value of ΔS_M, which depends on the derivative $\partial I/\partial T$ (see the formula). The temperature at the inflection point is close to the Curie point of the given alloy.

The results of the calculation of the temperature dependence of the magnetic part of the entropy $\Delta S_M(T)$ for various Gd_xDy_{1-x} alloys are shown in Fig. 1. From the form of these curves one can judge the efficiency of the working substance prepared from the corresponding compound. From the form of the curves of $\Delta S_M(T)$ it follows that ΔS_M reaches its maximum value at different temperatures that depend linearly on the concentration of Dy in the compounds. This result is easy to understand if we recall that Dy has an antiferromagnetic–paramagnetic transition temperature of 180 K, whereas the Curie temperature of gadolinium is 293 K.

The maximum values of ΔS_M are about the same for the various compositions. This is because the jump in the magnetic part of the entropy of pure Gd and pure Dy at their Curie points are about the same and the substitution of atoms of one element with atoms of the other in the compound does not change these quantities.

The experimental data that we obtained were analyzed numerically to provide essentially a comparison of the values of ΔS_M at fixed temperature for alloys with various concentrations of Dy and Gd. The concentrations of the rare-earth metals in the working substance could be varied by changing the number of plates prepared from the corresponding alloy in the composite working substance or by some other method.

From our experimental data for the alloys mentioned above we calculated $\Delta S_M(T)$ of the composite working substance consisting of plates prepared from the compounds (see Fig. 2, curve 1). From the analysis we concluded that the cooling agent $Gd_{0.59}(Gd_{0.90}Dy_{0.10})_{0.41}$ is the most promising one for use in magnetic refrigerators. We also studied this working substance experimentally. The sample in this case was a plate of Gd and a $Gd_{0.90}Dy_{0.10}$ alloy, with a mass of 16.50 and 11.25 mg, respectively. The experimental curves of $\Delta S_M(T)$ for the cooling agent $Gd_{0.59}(Gd_{0.90}Dy_{0.10})_{0.41}$ are shown in Fig. 2 by curve 2.

In summary, an analysis of the temperature dependences of $\Delta S_M(T)$, calculated for compounds with various concentrations of Dy has revealed the best material for use as the working substance. In choosing the working substance the principal factors taken into account were the value of $\Delta S_M(T)$ at the Curie point and the temperature region over which the value of ΔS_M remains high.

A comparison of the data for various concentrations of Dy in the Gd_xDy_{1-x} compounds showed that the combination $Gd_{0.59}(Gd_{0.90}Dy_{0.10})_{0.41}$ satisfied all the requirements for the working substances of refrigerator devices. It can be concluded the compound $Gd_{0.59}(Gd_{0.90}Dy_{0.10})_{0.41}$ is a promising one for use as the cooling agent for magnetic refrigerators operating at room temperature.

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Laser deposition of $YBa_2Cu_3O_x$ films on Si with a diffusion-stable buffer sublayer of ZrO_2

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The preparation of high-quality high-T_c superconducting films on semiconductor substrates, required for modern semiconducting and superconducting elements in microelectronics, is complicated by the strong interdiffusion of these materials.[1] It is possible to reduce the effect of diffusion by methods not involving annealing[2] by using high deposition rates[3] or low synthesis temperatures,[4] or by using an interlayer of a chemically inert material between the substrate and the film.[5] Films of $YBa_2Cu_3O_x$ on silicon with a critical temperature $T_c(R = 0) = 86$ K and a high current-carrying capacity were obtained by Fork et al.[6] just with the use of an epitaxial sublayer of ZrO_2.

We have studied how the conditions of formation of a buffer layer of ZrO_2 affect the diffusion stability and have shown that the method of homoepitaxy can be used to neutralize the interdiffusion of the high-T_c material and the silicon substrate.

The films of $YBa_2Cu_3O_x$ and the sublayers of ZrO_2 were grown by pulsed laser deposition by the non-annealing method with the use of two synchronized solid-state lasers operating at the wavelength 1.06 μm with a pulse length of 10 ns and a repetition rate of 50 Hz (Ref. 7). The energy density at the targets (high-T_c ceramic and metallic Zr, respectively) was 20-50 J/cm^2. The commercial silicon substrates were of the (100) orientation. The rate of deposition was 3-5 Å/s; the thickness of the high-T_c film was 1500-2000 Å, and of the Zr about 200 Å.

Direct deposition of the ZrO_2 sublayer by laser ablation of Zr with an oxygen partial pressure of 0.1 to 1 torr and the optimum substrate temperature (700-800°C) did not provide complete suppression of the interdiffusion of the high-T_c material and the silicon. The films obtained on this sublayer had an extended superconducting transition (Fig. 1, curve a). We associate this result with an amorphous SiO_2 layer on the Si surface and the formation of a polycrystalline film of ZrO_2 on this layer, with considerable diffusion of silicon occurring along the grain boundaries.

We were able to improve the diffusion isolation by a method based on homoepitaxy. The first layer of high-T_c superconductor (100-500 Å) was deposited at a reduced temperature (650°C), at which the diffusion of silicon is slow and the 123 phase that is formed is only slightly disordered. Then the temperature was raised to the optimum value (720-740°C) and the deposition was continued until the film had the desired thickness. In this case, even with deposition on a polycrystalline ZrO_2 prepared without removal of the native oxide SiO_2, the films had a relatively sharp superconducting transition (Fig. 1, curve b).

A substantial reduction of the diffusion in the high-T_c film is to be expected when a single-crystal coating of ZrO_2 is used, but to form such a film it is necessary to remove the native silicon oxide from the substrate and prevent the formation of SiO_2 while the silicon substrate is heated in the oxygen partial pressure necessary for the formation of the ZrO_2

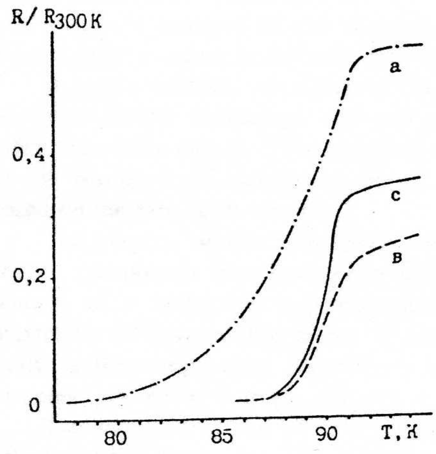

FIG. 1. Temperature dependence of the resistance of $YBa_2Cu_3O_x$ films prepared on ZrO_2/Si substrates. Curves normalized to the resistance at 300 K.

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