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Original article

Inclusions of metastable superconducting phase of gallium in $SmGa_2$

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ABSTRACT The magnetization M of the $SmGa_2$ compound has a paramagnetic character in a wide temperature range, and when the temperature decreases below 30 K, a significant increase in magnetization is observed, which indicates the formation of a magnetically ordered state. At temperatures below 5 K, a sharp feature is observed on the M(H) dependences, which is the contribution from the magnetization of superconducting submicron gallium inclusions. Analysis of the M(H) dependences measured at different temperatures below 5 K allowed us to assume the presence of two superconducting gallium phases. The critical temperature T_C = 5.9 K and the critical field H_C (0) = 560 Oe correspond to the formation of a metastable β-phase of gallium, and the critical temperature T_C = 8.4 K and the critical field H_C (0) = 1100 Oe can be associated with the formation of a thin layer of amorphous gallium on the surface of the β-phase inclusions.

KEYWORDS magnetization, superconductivity, microparticles, metastable phase, gallium.

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1. Introduction

Gallium is a component of many binary and multicomponent compounds, in particular such technically important compounds as the semiconductor GaAs and rare earth compounds with strong magnetic properties. In the study of gallium-containing compounds, it was discovered that in a number of cases, small particles of pure gallium precipitate, usually with a metastable β-Ga structure, having a critical superconductivity temperature T_C from 5.9 K to 6.2 K. In our work, we investigated the magnetic properties of the binary compound $SmGa_2$ and observed low-temperature features of magnetization associated with the presence of superconducting gallium inclusions in the compound.

2. Method

The $SmGa_2$ compound was obtained by the solution-melt method [1]. The sample was a intergrowth of small single crystals with dimensions of $3\times2\times0.5$ mm^3 and a mass of 20 mg. X-ray structural analysis confirmed the formation of the AlB_2 crystallographic structure and the absence of other phases (<2% by volume). The dependences of the magnetization M on the magnetic field H and temperature T were obtained using a vibration magnetometer of the PPMS setup (Physical Property Measurement System, Quantum Design), which is a system for measuring the physical properties of materials at low temperatures and in strong magnetic fields.

3. Results and discussion

The dependence of the magnetic moment M on the temperature T, shown in Fig. 1a, was obtained in the cooling mode in a magnetic field H = 300 Oe. The magnetization of $SmGa_2$ smoothly increases with decreasing temperature to T≈30 K, but the Curie-Weiss law is not satisfied. When the temperature T decreases below ∼30 K, a significant increase in magnetization is observed, which indicates the formation of a magnetically ordered state. A flattening of the dependence of the susceptibility on temperature below 5 K was observed, which corresponds to ferromagnetic ordering. The non-fulfillment of the Curie-Weiss law in the high-temperature (paramagnetic) region was observed in ref. [2] for $SmGa_2$ and is characteristic of samarium-containing compounds [3]. The increase in magnetization in the low-temperature region, associated with the formation of a magnetically ordered state, were also observed in [2].

Figure 1b shows the magnetic field dependences of the magnetic moment of $SmGa_2$ at temperatures T = 2–12 K. The dependence M(H) at T = 12 K is practically linear at H >5 kOe, and nonlinearity in low magnetic fields reflects the onset of ferromagnetic ordering. At lower temperatures, the nonlinear region expands up to maximal magnetic field. The magnetization values increased with decreasing temperature and only at the lowest temperature (T = 2 K) a slight decrease in M(H) was observed in high field, as in [2]. In general, the features of the temperature and field dependences of the magnetic moment are in good agreement with the results of ref. [2] at T > 5 K.

At T $\leq$ 5 K, an unusual feature is observed in the dependence M(H) in the region of low fields. This feature is shown on an enlarged scale for T = 5 K on Fig. 1b (upper inset). The lower inset shows that at a higher temperature T = 6 K this feature is not observed, and the dependence M(H) demonstrates a small ferromagnetic loop.

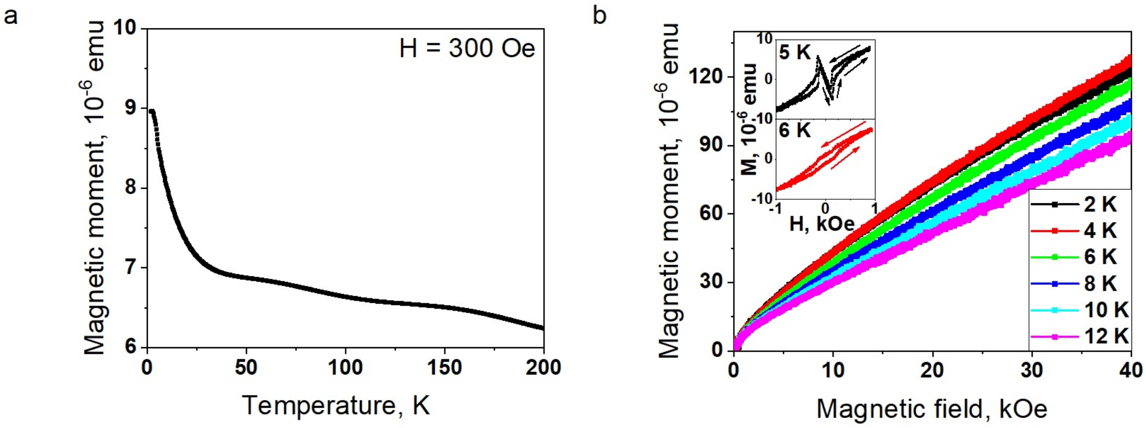

FIG. 1. Dependences of the magnetic moment M on (a) temperature T in magnetic field H = 300 Oe and (b) on the magnetic field at temperatures T = 2–12 K in the $SmGa_2$ compound. The insets to Fig. 1b show the region up to H $\approx$ 1 kOe at T = 5 and 6 K, the arrows indicate the direction of the magnetic field changes

Figure 2a shows the ΔM(H) dependences at temperatures T $<$ 6 K up to the region of magnetic fields H $\approx$ 1 kOe, where the ΔM(H) values were obtained by subtracting a small ferromagnetic hysteresis loop M(H,6K) from the measured M(H,T) dependences at these temperatures. The obtained dependences of the magnetic moment ΔM(H) are weakly hysteresis loops typical for type I superconductor and connected with submicron inclusions of pure gallium in the $SmGa_2$ compound, and the critical parameters of the superconducting phase of gallium can be determined.

Gallium exhibits a high degree of polymorphism with one stable orthorhombic phase (α-Ga) [4, 5] and several metastable phases (β, γ, δ, ε) [6, 7] at atmospheric pressure and additional phases (Ga-II, Ga-III and Ga-V) under pressure [8, 9]. Many of these phases are superconducting (α, β, γ, δ, ε and Ga-II). The metastable β-Ga phase has a monoclinic structure, and shows transition to the superconducting state at temperatures ranging from 5.9 K to 6.2 K [10–12].

An analysis of the ΔM(H) dependences (Fig. 2b) allows us to determine the phase of the superconducting gallium inclusions in the $SmGa_2$ sample. In general, the ΔM(H) dependence is similar to the weakly hysteretic dependence of the magnetization of a type I superconductor (which should be expected for submicron gallium inclusions), but the sharp break in the descending branch of the dependence allows us to assume that there is a superposition of individual dependences from two superconducting phases of gallium.

In the ΔM(H) dependences, one can distinguish two characteristic magnetic fields H_{C1} and H_{C2} (indicated by arrows in the inset to Fig. 2a). The field H_{C1} was determined by extrapolation of linear decreasing path of M(H) dependence, the field H_{C2} was determined as the field of the beginning of magnetic hysteresis. The values of these fields can by determined with the accuracy $\pm$ 5 Oe. Taking into account that the dependence of the critical magnetic field of the superconductor H_C can be represented as $H_C(T) = H_C(0)\left(1 - \left(\frac{T}{T_C}\right)^2\right)$, Fig. 2b shows the dependences of the critical magnetic fields H_{C^1} and H_{C^2} on the square of the temperature $H_C(T^2)$. Extrapolation of these dependences to H = 0 leads to two critical temperatures T_{C^1} = 5.9 $\pm$ 0.1 K and T_{C^2} = 8.4 $\pm$ 0.1 K.

The first critical temperature T_{C^1} = 5.9 K can naturally be associated with the formation of the metastable phase β-Ga, in which gallium microinclusions in gallium-containing compounds usually crystallize and which has a T_C in the range from 5.9 K to 6.2 K [9–11]. Additional evidence in favor of the formation of this phase is the coincidence of the measured dependence $H_{C^1}(T^2)$ (black dots and dotted line in Fig. 2b) with the dependence $H_{C^1}(T^2)$ obtained in [11] for β-Ga (blue solid line in Fig. 2b).

The second critical temperature T_{C^2} = 8.4 K can be associated with the formation of the amorphous phase of gallium, which, according to [13], has T_C = 8.5 K. This amorphous phase of gallium can be formed as a thin layer on the surface of β-Ga inclusions, the formation of individual inclusions of the amorphous phase is unlike, since, as shown in [13], the amorphous phase formed during irradiation of thin gallium films at T = 4 K crystallizes into the β-phase already upon heating to 16 K. Another possibility is the additional formation of gallium particles in the metastable γ phase, which, as shown in [10], has a critical temperature of T_C = 7.6 K and a critical field of H_C(6.3K) = 600 Oe , which is close to the extrapolated values of H_{C^2} at this temperature.

The formation of small superconducting inclusions of gallium (in most cases, the metastable β-Ga phase [6, 7, 10–12, 14]) was observed for a number of gallium-containing compounds obtained by different methods:

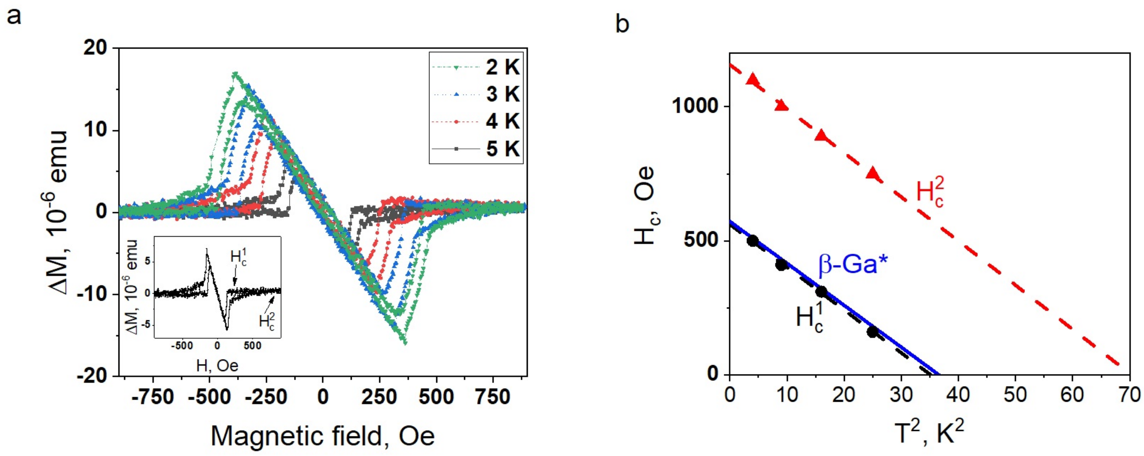

FIG. 2. (a) Dependence ΔM(H) = M(H,T) – M(H,6K) at H≤1 kOe and temperatures T = 2–5 K. The inset shows the dependence ΔM(H) at T = 5 K, the arrows indicate the critical magnetic fields H_{C^1} and H_{C^2}. (b) Dependences $H_{C^1}(T^2)$ and $H_{C^2}(T^2)$ – dots – experiment, dotted line – extrapolation, and blue solid line – literature data for β-Ga* [12]

- In rare earth compounds with gallium, for example, in YbGa$_5$, superconducting properties below $T_C \approx 2$ K were observed during magnetic measurements, associated, as the authors believe, with Ga filaments formed at grain boundaries [15].
- In GaN compounds doped with transition metals (Fe, Cr, Mn), superconducting properties with $T_C \approx 6$ K and $H_C \approx 600$ Oe were observed, associated with gallium clusters [16].
- In gallium oxide Ga$_2$O$_3$ films with a large oxygen deficiency, Ga clusters are formed with a superconducting transition temperature depending on the size of the Ga inclusions [17, 18].
- In gallium-doped Si films, gallium nanoinclusions exhibited superconducting properties at temperatures T≤7 K [19].

In some cases, the observation of superconductivity in gallium-containing compounds may also be associated with the formation of inclusions of superconducting phases of pure gallium, since the critical parameters of these compounds (T_C and H_C) are close to the values characteristics of gallium phases. Thus, one can note reports on the superconductivity of the GeGa compound with $T_C \leq 6$ K and $H_C(0) \approx 7$ kOe [20], the AGa$_x$Si$_{2-x}$ (A = Sr, Ba, Ca) compound with T_C = 4.4–5.2 K [21], and the semiconductor compounds GaSb and GaAs with $T_C \approx 10$ K [22]. Earlier, there were cases when superconductivity was reported in compounds, which, as further analysis showed, was associated with metal microinclusions, for example, in InN compounds with inclusions of superconducting indium [23].

4. Conclusion

Thus, the measurement of the magnetization of the SmGa$_2$ compound showed that in a wide temperature range the dependence M(T) has a paramagnetic character, not obeying the Curie-Weiss law. When the temperature decreases below 30 K, a significant increase in magnetization is observed, which indicates the formation of a magnetically ordered state. At T = 12 K, the dependence M(H) in magnetic fields $H \geq 10$ kOe is almost linear. At lower temperatures, the dependence M(H) becomes increasingly nonlinear, and upon transition to the lowest temperature T = 2 K, a slight decrease in magnetization in high fields is observed.

At $T \leq 5$ K, the M(H) dependence exhibits a feature in the low-field region, which is a contribution from the magnetization of superconducting submicron gallium inclusions. The critical temperature T_C = 5.9 K and the critical field $H_C(0)$ = 560 Oe correspond to the formation of a metastable β-phase of gallium. The second critical temperature T_C = 8.4 K and the critical field $H_C(0)$ = 1100 Oe can be associated with the formation of a thin layer of amorphous gallium on the surface of the β-phase inclusions or formation of the metastable γ-Ga particles. The formation of gallium inclusions in gallium-containing compounds is a frequently observed effect and can be detected in low-temperature magnetic measurements.

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