Anomalous Low Resistivity at Room and Elevated Temperatures of Manganin Alloy Implanted with High Dose Niobium Ions

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(Received August 8, 2011; in final form September 17, 2011)

The anomalous low resistivity metallic material at room temperature has been discovered. Known high resistive material called manganin in form of 10 μ m thick foil was one side implanted with high dose of niobium ions of 2.5×10^{17} Nb ions/cm² and then with 2.5×10^{13} Kr ions/cm². Before and after implantation procedure investigated manganin foils were temperature treated in 130 °C during 100 h. Basic resistance measurements were performed just after implantation observing large decrease of its resistivity. In repeated measurements after long time later (about twelve months), at temperature of 22 °C, practically no resistivity was measured. Four-terminal method for resistance measurements was used.

PACS: 72.15.Eb

1. Introduction

Superconducting phenomenon is a very interesting problem from scientific point of view and, on the other hand, has very important meaning for practical applications [1]. Superconductors with critical temperature close to room temperature, not discovered yet, seem to be an ideal solution for electrical energy transporting problem. In our high pressure investigations [2] high resistive alloy called manganin [3] as a high pressure sensor has been widely used. Firstly manganin was used in high pressure metrology by Bridgman in 1912. Manganin is also being used as resistance thermometer of low temperature (10–250 K). First of all that alloy is used for fabrication of standard resistors, shunts and constructional resistor elements. Manganin was firstly developed by E. Weston (1892) and produced by Isabellen Hutte in 1899. Up to now is produced with great market success. Nominal content of manganin is 87%Cu, 11%Mn, 2%Ni as well as some miniscule amounts of other components which are a know-how secret. Manganin is a solid solution (substitution alloy) of Mn and Ni in Cu, with insignificantly deformed copper lattice.

Commercially available manganin products have small grain polycrystalline structure with the same texture due to its plastic deformation technology. Since years 2000 the manganin was a subject of investigation for us with use of implantation technique. The aim of this investigation was to improve its thermoresistance characteristics (should have almost zero temperature sensitivity in temperature close to room temperature and have as small as possible thermal electromotive force against copper). The authors' knowledge about high temperature superconducting phenomenon is a basic one as they have not carried out any scientific work in this field as yet. But earlier the resistance–temperature characteristics of specimens, after implantation were checked in low temperature up to 4.2 K.



Fig. 1. Temperature dependence of relative changes of manganin resistivity from 4.2 K to 1100 K.

The example of measurement is shown in Fig. 1. In manganin specimens implanted with krypton, xenon, bismuth, carbon, titanium, no superconducting effect was noted. Interesting phenomenon with manganin implanted with high dose niobium ions appearing of anomalous low resistivity at temperature up to 40 °C has been observed.

2. Experimental setup

As we mentioned above well known resistive material called manganin in form of 10 μ m thick foil was used in our investigations. The planar dimensions of specimen 22 × 2 mm² were obtained from large dimension foil using laser cutting technique in Tele and Radio Research Institute in Warsaw. The implanted surfaces remained as made by producer i.e. Isabellen Hutte (Germany). Specimens were on one side high dose implanted by niobium ion of 2.5×10^{17} Nb ions/cm² with energy of 30 keV and then with krypton ions with dose 4×10^{13} Kr ions/cm² and energy of 245 MeV. Niobium implantation has been

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performed in Moscow Lomonosov State University and next krypton implantation in Joint Institute for Nuclear Research in Dubna, near Moscow. Before and after the implantation procedure, investigated manganin foils were temperature treated in 130 °C by 100 h in pure silicon oil and then carefully cleaned using methyl alcohol as cleaners. Full technological information concerning implantation procedure was obtained using SUSPREVI.8 code [4] with exponential fill model of "high dose effect".



Fig. 2. SUSPREVI.8 code depth profile of manganin samples implanted with Nb⁺ ions of 2.5×10^{17} Nb ions/cm² dose with energy of 30 keV.

The concentration of implanted niobium atoms in manganin specimens is shown in Fig. 2 only.



Fig. 3. Depth profile of krypton atoms in hypothetic large dimensions of manganin material obtained using SUSPREVI.8 code. Dose -2.5×10^{13} Kr ions/cm² and energy – 245 MeV.

The same calculation but for Kr ions is presented in Fig. 3. As we can see, the theoretical implantation range of Kr ions was much larger than the thickness of specimens, so its use here was mainly for achieving recoil implantation. Thin copper wire of 0.05 mm in diameter was soldered to the ends of specimen.

Four-terminal method for resistance measurement was used. A common thin soldering alloy and soldering paste was used. In some case when investigation in very low temperature was predicted an indium as solder was used. The soldering was made principally on the implanted side of specimen. Some moistening by soldering material of the surface not implanted by niobium was possible. Also terminals do not exactly fulfill theoretical conditions as current and voltage terminals are not separated. That means that some disturbances in correct resistance measurement of specimens could be expected. Therefore also another arrangement has been used. Two contacting voltage terminal with controlled pressure and with distance between them 15 mm was used. For two current terminals, soldered to specimen ends wires were used. The typical, universal, measuring instrumentation, of FLUKE (8846A) production, was used.

Basic resistance measurements of implanted specimen were performed just after implantation observing large decrease of its resistivity. In repeated measurements after a long time, at temperature of (20-40) °C, practically no resistivity was discovered but the Meissner effect was not observed.

3. Measurement of specimen resistance

The specimen used in experiments presented here is shown in Fig. 4. We should consider following structure of measured resistance: $R_{\rm specimen}$, to be found, $R_{\rm inter} = 0.046 \ \Omega$ — resistance of intermediate wire connector and $R_{\rm cable} = 0.357 \ \Omega$ — the resistance of the cables supplied to the FLUKE multimeter. The measurements were performed using two systems: two-terminal and four-terminal system. All different combinations with terminals were done. In all cases the results were the same with maximum uncertainty of 0.0015 Ω for two terminals and 0.0005 Ω for four terminals.



Fig. 4. Resistance measurement device: $R_{\rm specimen}$ — specimen resistance, $R_{\rm inter}$ — intermediate wire connection, $R_{\rm cable}$ — resistance of the multimeter cable and the photo of investigated specimen placed on the isolation plate. Arrows present the contact voltage terminals.

The results of our measurement of specimen resistance are the following: $R_{(\text{twoterminals})} = (0.4171 \pm 0.0015) \Omega$ and $R_{(\text{fourterminals})} = (0.0062 \pm 0.0005) \Omega$. To this reading some value due to the previously mentioned small thin elements between current and voltage terminals is included. For contacting voltage terminals we have obtained following results: $R_{(\text{twoterminals})}$ equal to 0.4170 Ω and for four-terminal method — 0.0035 Ω . That last value adopted to 22 mm specimen length gives specimen resistance value of $(0.0051 \pm 0.0005) \Omega$. The observed difference 0.0011 Ω is understandable, see above text.

Calculated resistivity, for all interesting us cases, is the following: for manganin used in our experiments — 44 $\mu\Omega$ cm, for pure copper — 1.72 $\mu\Omega$ cm (at 4.2 K — 2.0 n Ω cm — literature data [5]), for mean value of implanted specimen — 0.35 $\mu\Omega$ cm, for strongly implanted layer — using simplest calculation — 0.0006 $\mu\Omega$ cm and for strongly implanted layer, using special method [6] for more accurate interpretation of implanted flat specimens — 0.0009 $\mu\Omega$ cm. We may conclude that the resistivity of manganin after implantation procedure applied in our investigation has been decreased by about 50 000 times and is about 2 times lower than residual copper resistivity.

4. Summary

The obtained effect was rather unexpected. The origin of the anomalous low resistivity, in observed by us Nb implanted manganin specimens, have an unknown yet character. Because the observed phenomenon is not a superconductivity, what is its nature is difficult now to say. Further fundamental research will be undertaken.

After other investigations, up to now carried out by the authors, there remained only one specimen, so no destructing method of its investigation is predicted in the near future. For some time the specimen will be attainable only for persons interested in visual observation and resistance measurements. In the authors opinion there exists, in the foil, looking from implanted side, in depth of 12 nm, unique of very low resistance chemical component, in which niobium atoms play a fundamental role.



Fig. 5. The simplex model of anomalous low resistivity, niobium implanted, manganin. Red circles present copper atoms, blue — niobium, black — manganese and yellow — nickel.

We can expect the existence of a very damaged, complex structure of 21×10^{21} Cu ions/cm³, 31×10^{21} Nb ions/cm³, 2.5×10^{21} Mn ions/cm³ and 0.4×10^{21} Ni ions/cm³, having thickness about 20 nm and having no crystallographic or chemical ordering (see Fig. 5). In the whole volume of this structure, because implantation is homogeneous in planar sense, the "superconducting lines" (surfaces, layers) can exist in the specimen, so electrical charge transporting can easily take place. The importance of our discovery can be easily concluded, especially since manganin alloy is cheap and its technology is well developed. Niobium is also a not too expensive material and implantation technology is very well developed in some countries. The implantation of krypton ions, from the point of view of anomalous high conductivity, might have no essential meaning. Nevertheless if it is necessary it can be performed with much smaller energy, maybe of an order of 50 keV. For such a situation a normal implanter can be used.

Appendix Temperature and current dependence

It was very interesting to know the behavior of discovered material at extended over room temperature and different current density. From repeated Ohm's experiment we have obtained slightly decreased value of specimen resistance with current (see Fig. 6). Assuming that current is flowing through implanted part of specimen maximum current density used was calculated as 5 kA/mm^2 . We can say that this experiment confirms their ohmic character. On the other hand, experiment resistance–temperature curve presented in Fig. 7 gave information that resistivity of specimen is constant or somewhat decreases with temperature. Maximal temperature 40 °C is high enough to expect its proper application in open space laboratory, natural environments, where temperature increase up to 40 °C is almost sure.



Fig. 6. Resistance–current characteristics of investigated specimen at temperature 22 °C.



Fig. 7. Resistance–temperature characteristics of investigated specimen. Observed irregularities are connected with outside disturbances. Red squares — data for decreasing temperatures.

Acknowledgments

Authors thank to Prof. Alexander Didyk and Dr. Viera Semina from JINR Dubna for long time cooperation with us and for Kr implantation, to Moscow State University for niobium implantation, to Prof. Krzysztof Wieteska, director of IAE POLATOM for his help in many live aspects, to science contact manager of Isabellen Hutte for gratuitous manganin foils.

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