Superconducting Properties of Atomic-Disordered Compound MgCNi$_3$

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(Dated: November 21, 2018)

The effect of radiation-induced disordering in a nuclear reactor (fast neutrons fluence $\Phi = 5 \times 10^{19}$ cm$^{-2}$, $T_{irr} = 340$ K) on resistivity $\rho$, superconducting transition temperature $T_C$ and upper critical field $H_{C2}$ of polycrystalline MgCNi$_3$ samples was investigated. It was found that $T_C$ decreases under irradiation from 6.5 to 2.9 K and completely recovers after annealing at 600 °C. Temperature dependences $\rho(T)$ are characteristic of compounds with strong electron-phonon interaction. The $dH_{C2}/dT$ behaviour testifies to a considerable decrease in density of electronic state at Fermi level $N(E_F)$ in the course of disordering.

Radiation-induced disordering caused by irradiation with high-energy particles is a unique method of investigating the properties of superconducting and normal states of ordered crystals $^{[1, 2]}$. Even in broad-band metals, such as intermetallic compounds with A15 structure, long-range ordering loss leads to considerable rearrangement of the electronic spectrum, resulting in disappearance of individual features of the electronic structure. Disordering causes decrease in densities at Fermi level $N(E_F)$ and respective noticeable drop of $T_C$ in compounds with high initial $N(E_F)$ (Nb$_3$Sn or V$_3$Si), and considerable (from 1.5 to 7 K) rise of $T_C$ in compounds with low $N(E_F)$ and $T_C$ due to growth of $N(E_F)$ (Mo$_3$Si and Mo$_3$Ge) $^{[3, 4, 5]}$. In type HTSC compounds, disordering leads to more significant changes in properties: fast and complete $T_C$ degradation is accompanied with $N(E_F)$ decrease and metal-insulator transition $^{[6]}$. Thus investigation of response of a system to radiation-induced disordering serves as a kind of a test to reveal the characteristic features of its electron states. It was shown in recent papers $^{[6, 7]}$ that $T_C$ drop from 38 to 5 K observed at MgB$_2$ under radiation-induced disordering is connected mainly with considerable drop of $N(E_F)$, similar to Nb$_3$Sn or V$_3$Si compounds. In our investigation, we concentrated on the effect of disordering on the properties of superconducting compound MgCNi$_3$ ($T_C \sim 8$ K) with perovskite cubic structure of type SrTiO$_3$, unconventional for intermetallics $^{[8]}$. Our interest in this system was explained by the fact that its ground state is close to ferromagnetic due to the presence of a narrow peak in $N(E)$ located 45 meV below the Fermi level $^{[9]}$. This allowed us to regard it as a candidate for an unconventional (possibly triplet) superconductivity, similar to Sr$_2$RuO$_4$ compound. It is known that in Sr$_2$RuO$_4$, as distinct from conventional superconducting compounds (intermetallics), $T_C$ undergoes anomalously strong suppression even under a slight disorder $^{[10]}$. In MgCNi$_3$, maximum $T_C$ is achieved at excess of carbon content only (nominal composition MgC$_{1.5}$Ni$_3$), even though, according to neutron diffraction study, the actual composition is closer to Mg$_{0.96}$CNi$_3$, and excess carbon occupies the region between sample grain boundaries $^{[11]}$.

In the sample preparation, fine powders Mg, C and Ni with purity better than 99.5% were used as starting materials. The mixtures of appropriate composition were pressed into pellets; the pellets were wrapped in Ta foil and enclosed in an evacuated quartz tube, placed in a furnace, heated to 950 °C at a rate of 150 °C/h and kept at this temperature for 5 h, followed by furnace-cooling to room temperature. The highest $T_C = 6.5$ K and the best superconducting transition corresponded to the nominal composition $x = 1.45$ $^{[12]}$. Samples 0.5 × 1 × 5 mm$^3$ in size were irradiated with fast neutrons at $T_{irr} = (330 \pm 10)$ K, then annealed during 20 min at temperatures $T_{ann}$ from 100 to 600 °C in step of 100 °C. Resistivity $\rho(T)$ in fields up to 13.6 T was measured using a standard four-probe method.

The initial sample resistivity curve of transition to superconducting state (Fig. 1) is stretched in the direction of higher temperatures, onset is about 8 K. Mean transition temperature is 6.5 K. We defined the superconducting transition temperature $T_C$ as the temperature exhibiting half of the normal-state resistivity. Irradiation leads to $T_C$ drop to 2.9 K, and transition becomes narrower. Annealing at 500 °C almost completely recovers the initial form of dependence $\rho(T)$, while after annealing at 600 °C, transition becomes more abrupt with a higher $T_C = 7.1$ K compared with the initial sample.

Temperature dependences $\rho(T)$ of the initial, irradiated and isochronally annealed MgCNi$_3$ samples (Fig. 3) present curves with saturation, typical of the systems with strong electron-phonon interaction of types Nb$_3$Sn or V$_3$Si $^{[8]}$. A rather large value of residual resistivity $\rho_0 = 0.137$ mOhm cm (found by $\rho$ extrapolation to $T = 0$) of a sample in the initial state testifies to an insufficient degree of ordering. The absolute value of $\rho(T)$ approximately coincides with the data in $^{[8]}$ and is three times higher than in $^{[8]}$, even though temperatures dependences $\rho(T)$ are practically

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FIG. 1: Temperature dependences of reduced resistivity $\rho/\rho_0$ of initial MgCNi$_3$ sample (1), sample irradiated under fast neutrons fluence $\Phi = 5 \cdot 10^{19}$ cm$^{-2}$ (2) and sample annealed at $T = (100 - 600)$ °C during 20 min. (3 - 8). Solid lines are drawn across experimental points.

FIG. 2: Temperature dependences of MgCNi$_3$ sample resistivity $\rho(T)$; for designations, see Fig. 1. Solid lines present the calculation using expression (7).
FIG. 3: Temperature dependences of upper critical field $H_{C2}$ for MgCNi$_3$ sample; for designations, see Fig. 1. Solid lines are drawn across experimental points.

identical in all cases. Evidently, after irradiation and subsequent annealing at 600 °C, further ordering and residual resistivity drop to $\rho_0 = 0.124$ mOhm-cm occur in the sample.

The upper critical field $H_{C2}$, as determined from the half-transition temperature (0.5 of the normal-state resistivity), has a form typical of second-order superconductors (Fig. 3), the initial sample value of $dH_{C2}/dT$ is in good agreement with the data of paper [13]. A relatively weak change in the slope of $dH_{C2}/dT$ should be noted; a very similar behaviour at disordering was observed for MgB$_2$ [6]. So, for dirty superconductor

$$(-dH_{C2}/dT)_{\text{dirty}} = \left(8ek_B/\pi\right)(1 + \lambda)N(E_F)\rho_0,$$

the relatively weak change in $dH_{C2}/dT$ (Fig. 3) would evidently be compensated by a considerable (about 2.5 times) decrease in $N(E_F)$.

Deviations from the Block-Grüneisen law

$$\rho(T) = \rho_0 + \lambda_{tr}F_{BG}(\theta/T),$$

defining linear behaviour of $\rho(T)$ at high $T$, where $\theta$ is Debye temperature, $\lambda_{tr}$ is electron-phonon interaction constant proportional to parameter $\lambda$ in the McMillan expression for superconducting transition temperature

$$T_C \sim (\omega_{\text{in}}/1.2)\exp\left\{-1/(1 + \lambda)/(\lambda - \mu)\right\}, \quad \mu \sim 0.1,$$

are often described by an empirical expression

$$1/\rho(T) = 1/\rho_{\text{sat}} + 1/(\rho_0 + \lambda_{tr}F_{BG}(\theta/T)),$$

so $\rho(T)$ cannot exceed the value of saturation resistivity $\rho_{\text{sat}}$, which for type A15 intermetallics is about 0.2 mOhm-cm. Intuitive substantiation of (4) boils down to the fact that electron scattering becomes inefficient when the electron free path $l_{tr}$ becomes shorter than the Fermi wavelength, inversely proportional to wave-vector $k_F$; therefore, in the expression for conductivity $\sigma \sim (k_F)^2l_{tr}$, $l_{tr}$ should be substituted by a value close to $(k_F)^{-1}$. The interpolation formula $\sigma \sim (k_F)^2l_{tr} + k_F$ is equivalent to (4).

Fitting of experimental data on MgCNi$_3$ to expression (4), containing 4 fitting parameters $\rho_{\text{sat}}$, $\rho_0$, $\lambda_{tr}$ and $\theta$, yields good agreement with the close values of $\theta = (140 - 155)$ K. A similar fitting procedure for MgCNi$_3$ ($T_C \sim 8$ K) carried out in [12] with Einstein, instead of Debye, spectrum, yields the following parameters: Einstein temperature $\theta_E = 206$ K, $\rho_{\text{sat}} = 0.574$ mOhm-cm. The obtained value of $\theta$ is noticeably lower than that obtained in heat capacity measurements, Debye temperature $\theta_D \sim 235$ K [8]. However, using the value of $\theta = 150$ K and on the assumption of the Debye spectrum, we obtain $\omega_{\text{in}} = \exp(-1/3) \cdot \theta \sim 105$ K, which is considerably lower than $\omega_{\text{in}} \sim 480$ K for
Fig. 4: Upper critical field derivative $-dH_C/dT$ (left) and electron-phonon interaction constant $\lambda$ (right) for MgCNi$_3$ sample as a function of residual resistivity $\rho_0$. Solid lines present the calculation using expressions (8) and (4), respectively.

MgB$_2$ [14]. Expression (3) yields $\lambda \sim 0.8$, which compares well with the value of $\lambda \sim 1.1$ for MgB$_2$ [13]. Value $\lambda$ as a function of $\rho_0$ (Fig. 4) may be described with a linear dependence

$$\lambda = \lambda_0 (1 - (\rho_0/R)),$$

where $\lambda_0 = 0.92$, and $R = 0.85$ mOhm-cm.

The relatively large value of $\lambda$ (and hence, $\lambda_{tr}$) is generally in an agreement with significant nonlinearity of $\rho(T)$ characteristic of compounds with strong electron-phonon interaction. However, fitting parameter $\rho_{sat}$, varies significantly from 0.85 mOhm-cm for the initial sample to 0.5 mOhm-cm for the irradiated sample, which agrees poorly with the meaning of value $\rho_{sat} \sim (kF)^{-1}$, which must be constant in case of a broad-band metal.

The origin of $\rho(T)$ "saturation" for systems with strong electron-phonon interaction were analyzed in terms of the mean field theory in [15], where it was shown that (in case of a relatively weak coupling which does not lead to formation of a pseudogap) scattering rate is proportional not to the value of ions r.m.s. displacement $\langle u^2 \rangle$, but rather to $\langle (u^2)^{0.5} \rangle$, and so, in this case, instead of (2), we have

$$\rho(T) = \{(\rho_0)^2 + \lambda_{tr} F_{BG}(\theta/T)\}^{0.5},$$

which results in type $\rho(T) \sim T^{0.5}$ behaviour at high $T$. However, use of (6) fails to yield a satisfactory data description. The probable reason is that value $\lambda_{tr}$, in its turn, also depends on disordering (is characterized by a sum of static and thermal displacements), i.e., on $\rho(T)$; the same reason causes decrease in $\lambda$ with increase in $\rho_0$ (Fig. 4). Considering $\lambda_{tr}$ being in dependence on $\rho(T)$, similar to that of $\lambda$ on $\rho_0$ in (4), expression (6) is transformed into an equation

$$\rho(T) = \{(\rho_0)^2 + \lambda_{tr0}(1 - \rho(T)/R_{tr})(F_{BG}(\theta/T))\}^{0.5},$$

which, when solved for $\rho(T)$, yields the required expression, also containing four fitting parameters $R_{tr}$, $\rho_0$, $\lambda_{tr}$ and $\theta$. Expression (7) describes data with the same accuracy as expression (4), with similar values of $\theta$, but with almost equal fitting parameters $R_{tr}$ varying within (0.75 - 0.88) mOhm-cm. Such a good agreement between the values of $R$ in (5) and $R_{tr}$ in (7) does not look casual.

In conclusion, let us consider the probable causes of superconductivity degradation in MgCNi$_3$ under disordering. Loss of long-range order must lead to smearing of the fine structure of electron densities of state; at that, function $N(E)$ smoothes out, but without becoming zero. For superconductors with electron-phonon interaction, $\lambda \sim N(E_F)$, therefore $T_C$ should never go down exactly to zero; the latter requirement is evidently satisfied for the majority of compounds which may be related to broad-band intermetallics. A qualitatively different behaviour is observed in HTSC compounds: in all cases superconductivity is completely depressed at a much higher rate than in intermetallics, probably due to non electron-phonon mechanisms of superconductivity as well as to a proximity to metal-insulator transition [16].
Value $\lambda$ calculated by expression (3) decreases 1.5 times at MgCNi$_3$ under irradiation (Fig. 3), while the above value of $N(E_F)$ estimated using expression (1) decreases almost 2.5 times. Probably, such discrepancy in change of $\lambda$ and $-dH_{C_2}/dT$, as it was similarly supposed for, e.g., MgB$_2$ [8], may be due to the fact that the dirty limit of $l_{\sigma} \ll \xi$ is not reached in the given region. Coherent length $\xi$ may be estimated from the relation

$$\xi^2 = \Phi_0/(2\pi(-0.69dH_{C_2}/dT)T_C),$$

which yields $\xi = 55$ and 75 Å for the initial and the irradiated samples, respectively. Free path $l_{\sigma}$ may be estimated from an conventional expression used for conductivity

$$(\rho_0)^{-1} = (3\pi^2)^{-1/3}(e^2/\hbar)n^{2/3}l_{\sigma},$$

which yields $l_{\sigma} \sim 20$ Å for $\rho_0 = 0.137$ mOhm-cm (initial sample) and $l_{\sigma} \sim 8$ Å for $\rho_0 = 0.337$ mOhm-cm (irradiated sample). These relations of $l_{\sigma}$ and $\xi$ are definitely closer to the dirty limit. Further, expression (1) allows us to estimate $(-dH_{C_2}/dT)$ using the experimental values of $\gamma$ and $\rho_0$ or those obtained from band calculations $N(E_F)$. According to band calculations [9, 17, 18], $N(E_F) \sim 2.5$ (eV·spin-cell)$^{-1}$ = $2.8 \times 10^{37}$ (J·m$^{-3}$)$^{-1}$, using $\lambda \sim 0.8$, $\rho_0 \sim 0.1$ mOhm-cm, we obtain $(-dH_{C_2}/dT) \sim 3$ T/K, which is quite commensurate with the experimental value $(-dH_{C_2}/dT) \sim 2.5$ T/K. Thus there are probably no reasons to doubt the dirty limit applicability in the given case. Assuming $\lambda \sim N(E_F)$, using (1) and (5), we obtain the dependence

$$(-dH_{C_2}/dT)_{\text{dirty}} \sim \lambda(1 + \lambda)\rho_0 = \lambda_0(1 - (\rho_0/R))(1 + \lambda_0(1 - (\rho_0/R)))\rho_0,$$

(8)

shown as a solid line in Fig. 3. The causes of noticeable deviations at $\rho_0 > 0.25$ mOhm-cm are unclear, it should be noted only that very similar changes in $dH_{C_2}/dT$ at radiation-induced disordering were observed for MgB$_2$ [14]. Nevertheless, for MgCNi$_3$, the response to disordering is similar to that observed for conventional systems (intermetallics) with strong electron-phonon interaction.

Acknowledgments

Work supported by Minpromnauka, Russia (State Contracts No. 40.012.1.1.1150, No. 40.012.1.1.1146/Contract No. 15/02), Program of government support to leading scientific schools of Russia (Project No. 00-15-96581) and Russian Foundation for Fundamental Research (Project No. 01-02-16877).

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