

Magnetic and superconducting properties of $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$

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Samples with nominal composition $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ were synthesized and their magnetic and superconducting properties were investigated. $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ has a superconducting transition at $T_c=27$ K and an AFM one at $T_N=13$ K. It was established that the magnetic order is of a long range type. The coincidence of the obtained experimental value of the Curie constant and the theoretical one of the Ho-containing Mo-1212 shows that the magnetic properties of the samples are determined by the highly dominating phase Mo-1212. The double resistive SC transition, together with the absence of both diamagnetism and peak in the specific heat between the two critical temperatures denote the presence of granular superconductivity. The latter phenomenon and the observed Mo-deficiency can explain the low superconducting volume fraction of the samples.

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1. Introduction

After the synthesis of the ruthenocuprates $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10}$ (Ru-1222) and $\text{RuSr}_2\text{RCu}_2\text{O}_8$ (Ru-1212), (R = Sm, Eu, Gd) by Bauernfeind et al. [1] a coexistence of superconductivity (SC) and weak ferromagnetism (FM) was discovered in Ru-1222 (R=Eu, Gd) by the authors of [2] and in Ru-1212 [3]. It was established that the magnetic state of the Ru sublattice is not affected by the presence of the SC state, therefore the two states coexist in-trinsically on the microscopic scale. The authors of [4, 5] pointed out that the Ru ions in both Ru-1222 and Ru-1212 systems can be completely replaced by Mo ions. In Mo-1222 the SC competes with the magnetic order [4]. A coexistence of superconductivity and antiferromagnetism (AFM) in $\text{MoSr}_2\text{RCu}_2\text{O}_y$ for R=Y, Ho, Er and Tm was established in [5]. Up to now, less attention was drawn to this phenomenon in comparison with the coexistence of SC and FM in Ru-1212 and Ru-1222. The authors of [6] carried out a more detailed investigation of the Y-containing Mo-1212. They established that the AFM ordering, which coexists with the SC state through effectively decoupled subsystems, is not affected by the presence or absence of the SC state. Moreover, for the investigated samples the relation $T_c > T_N$ is valid. The purpose of the present work is to investigate and to discuss the SC and magnetic properties of Ho-containing Mo-1212.

2. Experimental details

Samples with nominal composition $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ were prepared by a solid state reaction from starting products Mo, Ho_2O_3 , SrCO_3 and CuO with a purity above 99.9%. They were mixed, homogenized, pressed into pellets and preheated at 750°C for 24 hours in air and sintered at 950°C for 24 hours in flowing oxygen. After regrinding and repressing sample A was synthesized at 1050°C and sample B - at 1080°C for 48 hours in flowing oxygen. Finally the two samples were annealed at 600°C for 48 h in flowing oxygen. X-ray diffraction (XRD) was used to examine the samples using a TUR-M62 diffractometer and CoK_α radiation. An EDS on SEM analysis was performed on the pellets using a SEM-525 Philips microscope combined with an EDAX 9900 device. The AC susceptibility and DC magnetization of the samples were measured by a SQUID magnetometer (Quantum Design: PPMS-9T and MPMS-XL7T). The resistance of the samples R vs. T was measured by the standard four probe method.

3 Results and discussion

In Fig. 1 the XRD patterns of samples A and B are given. They are similar to that of the Y-containing Mo-1212 and show the presence of a highly dominating phase 1212 (about 80%) and the non-superconducting SrMoO_4 as impurity. The calculated lattice parameters of the Mo-1212 phase in sample A are $a = 3.827 \text{ \AA}$, $c = 11.486 \text{ \AA}$ and those in sample B - $a = 3.837 \text{ \AA}$, $c = 11.511 \text{ \AA}$.

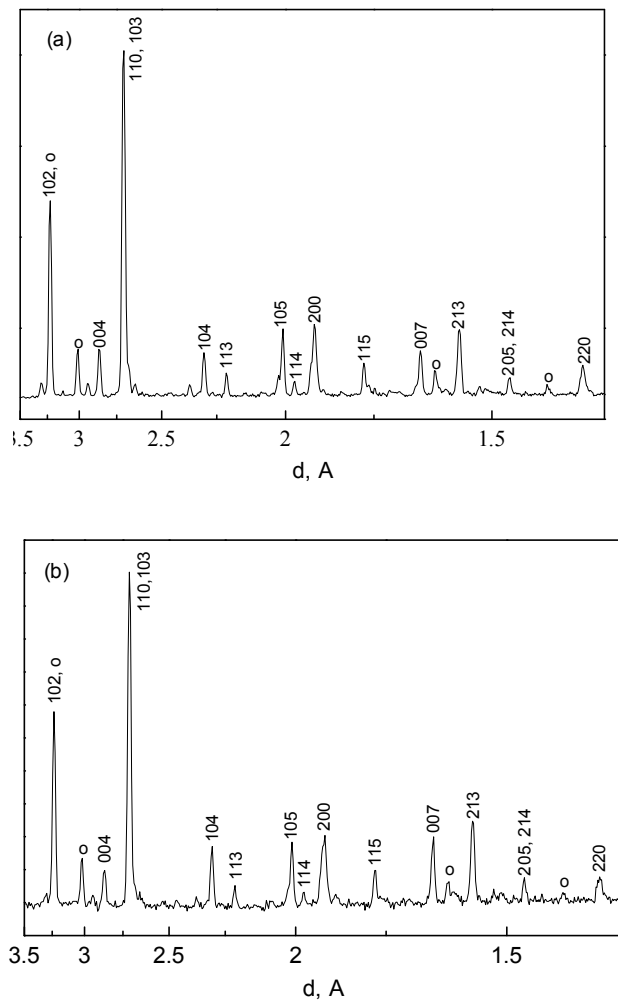


Fig. 1. XRD patterns of: (a) - sample A and (b) - sample B; o – SrMoO_4

Fig. 2 shows SEM pictures of both the samples. It can be seen that the average grain size is about $10\ \mu\text{m}$. Sample B contains more well-expressed tetragonal crystals in comparison with sample A. The EDS analysis showed that the chemical composition of the microcrystals of the dominating phase in sample A is $\text{Mo}_{0.5}\text{Sr}_{2.2}\text{HoCu}_{2.5}\text{O}_y$ and that of sample B - $\text{Mo}_{0.35}\text{Sr}_{1.9}\text{Ho}_{1.1}\text{Cu}_{2.8}\text{O}_y$. The observed deficiency of Mo is evidently due to its volatility. These formulae can be rewritten as $(\text{Mo}_{0.5}\text{Cu}_{0.5})\text{Sr}_{2.2}\text{HoCu}_{2.5}\text{O}_y$ and $(\text{Mo}_{0.35}\text{Cu}_{0.65})\text{Sr}_{1.9}\text{Ho}_{1.1}\text{Cu}_{2.15}\text{O}_y$, respectively. Therefore, we may suppose that the deficiency of Mo is compensated with Cu in the rocksalt layer of the phase 1212, as in the case of the (Pb,Cu)-1212 system [7]. This is confirmed by the increase of the lattice parameters of sample B because the Cu^{2+} ionic radius ($0.65\ \text{\AA}$) is greater than the Mo radii with octahedral or tetrahedral coordination ($0.41 - 0.64\ \text{\AA}$) [8]. Another argument in favor of this assumption is the presence of a highly dominating phase 1212 in the two samples.

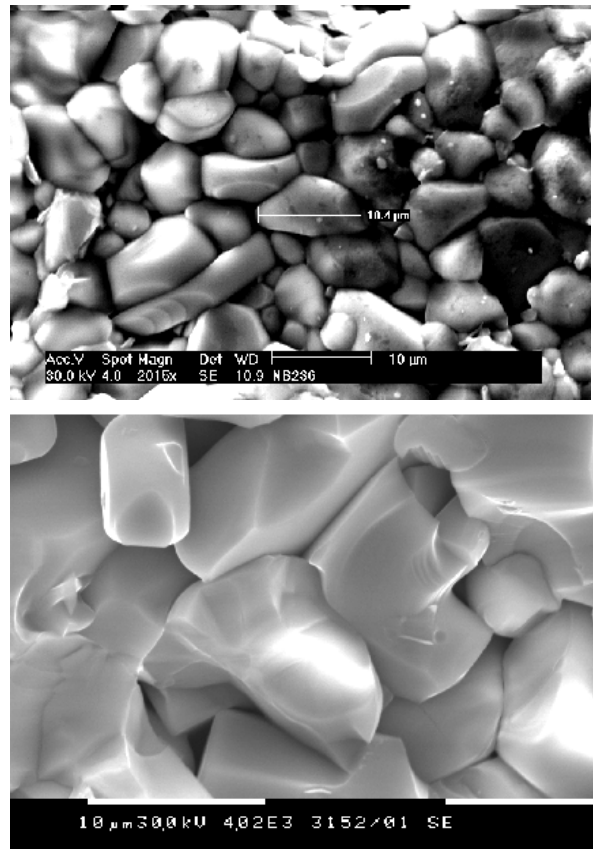


Fig. 2. SEM pictures of: (a) - sample A and (b) - sample B.

Fig. 3 shows the $\chi'(T)$ dependency of the zero-field cooled (ZFC) sample A at $H=0$. It has a SC transition at $T_c=27\ \text{K}$ and negative values of the susceptibility are observed below $T_d=18\ \text{K}$. The magnetic transition is expressed as a kink in the curve at $T_N=13\ \text{K}$.

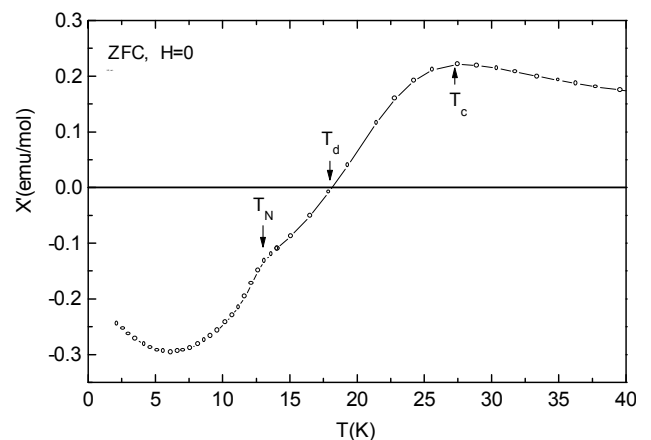


Fig. 3. $\chi'(T)$ dependency of a ZFC sample A at $H=0$.

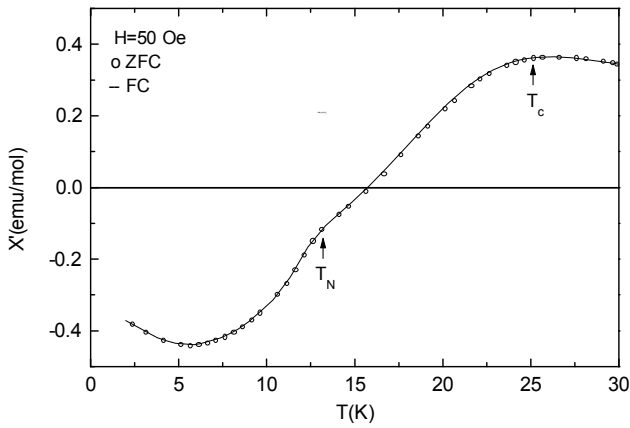


Fig. 4. $\chi'(T)$ dependencies of a ZFC and FC sample A at $H=50$ Oe.

In Fig. 4 we show the susceptibility curves of a ZFC and FC sample A at $H=50$ Oe. It may be seen that the two curves coincide, as in the case of the non-superconducting Yb-containing Mo-1222. For comparison, the ZFC and FC curves of all the investigated $\text{MoSr}_2\text{YCu}_2\text{O}_y$ samples are irreversible below T_N . Also the obtained value of T_N coincides with that of the non-superconducting Ho-containing Mo-1222 [4]. From the coincidence of the susceptibility curves of the ZFC and FC sample it is sufficient to conclude that the magnetic order is of a long range type [9].

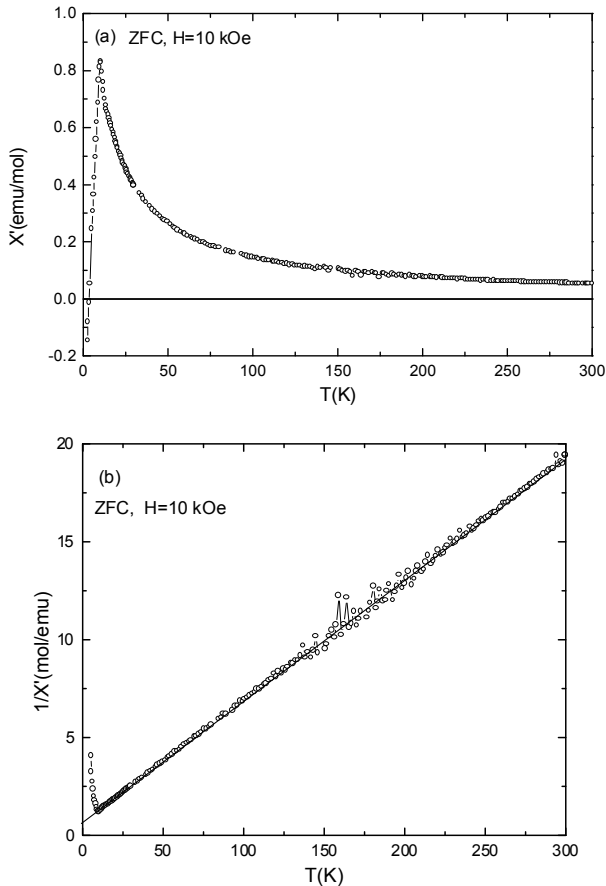


Fig. 5. (a) - $\chi'(T)$ dependency of a ZFC sample A at $H=10$ kOe and (b) - the respective $1/\chi'(T)$ dependency.

Fig. 5a shows the $\chi'(T)$ dependency of the ZFC sample A at $H=10$ kOe. The figure express that the negative values of χ' at low temperatures are still observed but no magnetic transition can be seen at this field. In Fig. 5b we show the respective $1/\chi'(T)$ dependency. A fit of the Curie-Weiss (CW) law is obtained above T_C according to the formula $\chi'=C/(T-\theta)$, where C is the Curie constant and θ is the CW temperature. The calculated experimental value of the constant is $C=16.22$ emuK/mol with a negative value of θ . The negative value of θ denotes the presence of AFM interactions. Since the Pauli paramagnetic SrMoO_4 does not contribute to the Curie constant [6, 10], the obtained value of C may be compared with the theoretical one of the Ho-containing Mo-1212. If one assume that the Mo ions are pentavalent with an effective magnetic moment of $1.73 \mu_B$, $4d^1$, $S=0.5$, as in the case of the Y-containing Mo-1212 [6] and, using the effective magnetic moments of Ho^{3+} ($10.89 \mu_B$) [11] and Cu^{2+} ($1.9 \mu_B$), the theoretical Curie constant of the Ho-containing Mo-1212 can be calculated.

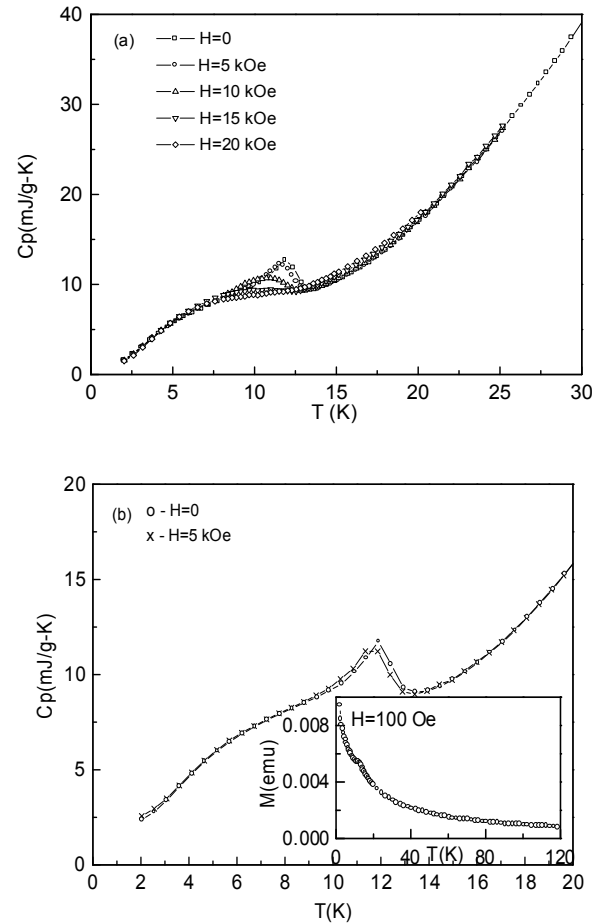


Fig. 6. (a) - Temperature dependencies of the specific heat of sample A at different fields; (b) - the same for the non-superconducting sample B at $H=0$ and 5 kOe. Inset: Temperature dependency of the magnetization $M(T)$ of sample B at $H=100$ Oe.

In our case it is found to be 16.136 emuK/mol. We also took into account the Mo-deficiency by using the

chemical composition of the micro crystals of the phase Mo-1212 in sample A - $\text{Mo}_{0.5}\text{Sr}_{2.2}\text{HoCu}_{2.5}\text{O}_y$. The coincidence of the theoretical and experimental values of the Curie constant shows that the observed magnetic properties of the samples are determined by the highly dominating phase Mo-1212.

In Fig. 6a the temperature dependencies of the specific heat of sample A at different fields are given. The curves show a specific heat peak at $T=12\text{K}\approx T_N$ and no specific heat anomaly at $T=T_c$ and higher temperatures is observed. The specific heat peak onset temperature is weakly dependant of the applied magnetic field. A reduction of the amplitude of the specific heat peak and a slight shift to the lower temperatures with increasing applied field are observed. A similar behavior of the $C_p(T)$ dependency is observed in Ru-1212 and Ru-1222 at $T=T_c$ by the authors of [12, 13]. In Fig. 6b the $C_p(T)$ dependencies of sample B at $H=0$ and 5 kOe are given. The curves also show a peak at $T\approx 12$ K. Taking into account that this sample is not superconducting (see the inset), we may conclude that the observed specific heat peak is related to the AFM transition of the investigated compound. This conclusion is also supported by the presence of peculiarity in the $M(T)$ dependence around 12 K (see the inset) for this sample.

Fig. 7 shows the $M(H)$ curve at $T=2$ K of sample A. The curve is linear up to about 8 kOe, which is typical for the AFM state. A small hysteresis at low fields can be seen in the inset. It may be associated with the Mo sublattice, as in the case of $\text{MoSr}_2\text{YCu}_2\text{O}_{8-\delta}$ [6]. The estimated superconducting volume fraction (svf) is 1.66% at $T=2$ K. This result confirms the lack of bulk superconductivity, established by the specific heat measurements.

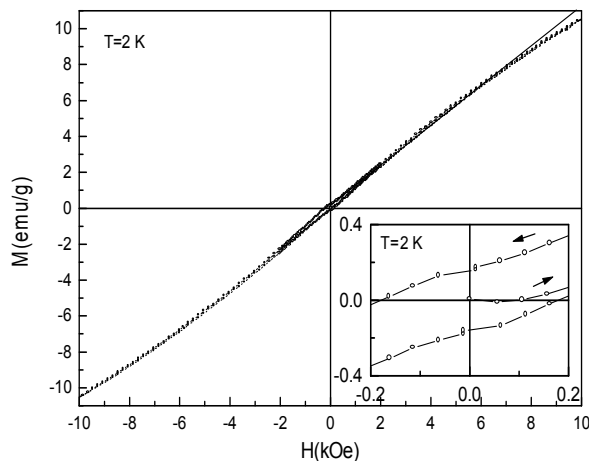


Fig. 7. Field dependency of the magnetization at $T=2$ K of sample A. Inset: an extended scale at low fields.

Fig. 8 shows the $R(T)$ dependencies of sample A at $H=0$ and 50 kOe. A broad SC transition at $T_{c1}\approx 30$ K with a second step at $T_{c2}\approx 22$ K can be seen at $H=0$. At $H=50$ kOe the SC transition becomes broader, T_{c1} decreases down to about 23 K and zero resistance is not achieved.

The two step resistive SC transition, together with the absence of

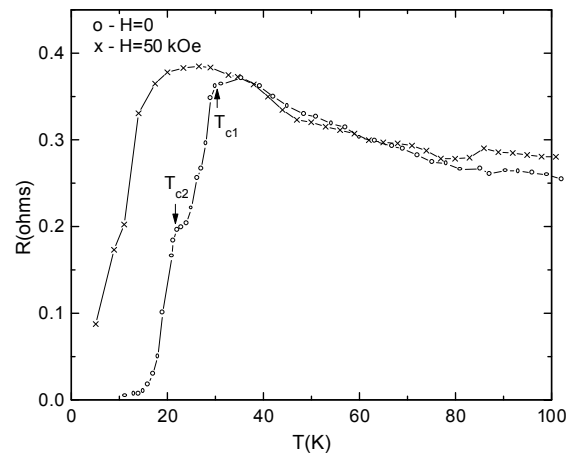


Fig. 8. $R(T)$ dependencies of sample A at $H=0$ and 50 kOe

both a diamagnetism and a peak in the specific heat at $T_{c2}<T<T_{c1}$ denote the presence of granular superconductivity [14]. This means that the superconducting properties are confined to small regions with a size comparable to the London penetration depth. Recently a similar phenomenon was observed in the magnetic superconductor Ru-1222 [15]. Another reason for the low svf of sample A and lack of superconductivity of sample B may be the deficiency of Mo in the both samples. This deficiency is compensated with Cu and with an increase of the extra oxygen atoms in the rocksalt layer of the phase 1212. However the oxygen in the (Mo,Cu)O layers due to a random arrangement tends to trap holes and prevents their transfer into the CuO_2 layers which carry the superconducting current. A similar phenomenon is observed in (Pb,Cu)-1212 system, when Pb is partially replaced by Sn [16].

4. Conclusions

Samples with nominal composition $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ were synthesized and their magnetic and superconducting properties were investigated. $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ has a superconducting transition at $T_c=27$ K and an AFM one at $T_N=13$ K. It was established that the magnetic order is of a long range type. The coincidence of the obtained experimental value of the Curie constant and the theoretical one of $\text{MoSr}_2\text{HoCu}_2\text{O}_{8-\delta}$ shows that the observed magnetic properties of the samples are determined by the highly dominating phase Mo-1212. The two step resistive SC transition, together with the absence of both diamagnetism and a peak in the specific heat between the two critical temperatures denote the presence of a granular superconductivity. The latter phenomenon and the observed Mo-deficiency can explain the low superconducting volume fraction of the samples.

Acknowledgements

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