Influence of Lu - substitution on the frustrated antiferromagnetic system $HoB_{12}$


**S. Gabáni[a], I. Baťko[a], M. Baťková[a], K. Flachbart[a*], E. Gažo[a], M. Reiffers[a], N. Shitsevalova[b], K. Siemensmeyer[c] and N. Sluchanko[d]**

[a] Institute of Experimental Physics, Slovak Acad. Sciences, SK-04001 Košice, Slovakia

[b] Institute for Problems of Materials Science of NASU, UA-03680 Kiev, Ukraine

[c] Helmholtz Zentrum Berlin, D-14109 Berlin, Germany

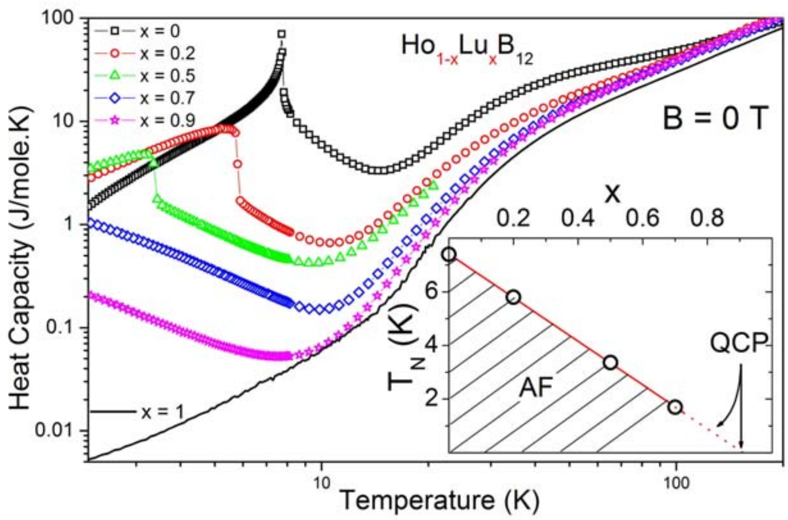
[d] General Physics Institute of RAS, RU-119991 Moscow, Russia



## Abstract

In this contribution we present results of experimental investigations of the geometrically frustrated metallic antiferromagnet $HoB_{12}$ (with ordering temperature $T_N$ = 7.4 K) influenced by substitution of magnetic Ho atoms through nonmagnetic Lu ones. In this case, in $Ho_{1-x}Lu_xB_{12}$ solid solutions, both chemical pressure and magnetic dilution take place with increasing content of Lu which changes the properties of the system. Experimentally, measurements of heat capacity and electrical resistivity of these solid solutions were performed from room temperature down to milikelvin temperatures and in magnetic fields up to 9 T. This wide range of experimental conditions allowed us among other things to follow the change of magnetic ordering temperature with concentration (x), i.e. to obtain the $T_N$ vs. x phase diagram. The received results show strong indications for the existence of a quantum critical point (QCP) close to $x_C \approx 0.9$. This critical point separates the region of magnetic order (starting with $HoB_{12}$ for $x$ = 0) and the nonmagnetic region (ending with superconducting $LuB_{12}$ for $x$ = 1).


**Graphical abstract**




Heat capacity of $Ho_{1-x}Lu_xB_{12}$ solid solutions in zero magnetic field. The inset shows the received ordering temperature ($T_N$) vs. concentration ($x$) phase diagram with a possible quantum critical point (QCP) at $x \approx 0.9$.

## 1. Introduction

Heavy rare earth (RE) dodecaborides ($REB_{12}$) have attracted considerable attention in recent years [see e.g. references 1, 2], above all due to the wide variety of their physical properties. They crystallize in the NaCl based fcc - structure, and their electronic and magnetic properties result mainly from electron occupancy of the 4f shell of rare earth ions. Among these RE dodecaborides one can find e.g., $LuB_{12}$ with a fully occupied 4f shell - a metal which becomes superconducting below 0.4 K [3], $YbB_{12}$ - an intermediate valence Kondo insulator [4, 5], and $DyB_{12}$, $HoB_{12}$, $ErB_{12}$ and $TmB_{12}$ [6, 7] - metals, which order antiferromagnetically in the Kelvin temperature range.

Recent intensive investigations of $HoB_{12}$, which is a metallic compound with a frustrated fcc crystal structure have shown that its magnetic structure exhibits rather complex features [8, 9]. The Curie-Weiss constant $\Theta$ of $HoB_{12}$ is about -24.3 K and its Néel temperature $T_N$ = 7.4 K. Three magnetic phases were observed below $T_N$ in the B vs. T phase diagram and well below $T_N$ the obtained neutron scattering results point to an incommensurate amplitude-modulated magnetic structure. Closely below $T_N$ the ordered state is highly degenerate. It was also shown that besides the dominating indirect exchange interaction of RKKY type also the dipole-dipole interaction and frustration effects of the fcc lattice seem to play an important role in the formation of its magnetic structure. In the paramagnetic region (at about 40 K) a Schottky contribution to heat capacity appears and can be interpreted as a manifestation of strong crystalline electric field. Moreover, above $T_N$ observed diffuse neutron scattering patterns indicate that at these temperatures (between about $T_N$ and $\Theta$) pronounced short range correlation (short range ordering) appears between neighboring magnetic moments of Ho-ions, similar as in low-dimensional magnets. Based on all received results it could be shown [9] that the geometric frustration in this compound is lifted in steps.

Thus, the substitution of magnetic Ho atoms through nonmagnetic Lu atoms in $Ho_{1-x}Lu_xB_{12}$ solid solution where both chemical pressure (as $Lu^{3+}$ ions are smaller than $Ho^{3+}$ ions) and magnetic dilution (as $Lu^{3+}$ ions are nonmagnetic) take place with the increasing content of Lu, presents an interesting way to study the change of $HoB_{12}$ properties. Moreover, there is a possibility to investigate the behavior of the $Ho_{1-x}Lu_xB_{12}$ system at / near the quantum critical point, which is formed when long-range magnetic order is suppressed to zero temperature (i.e. $T_N \rightarrow 0$ K) by tuning an external parameter, as e.g. by pressure, magnetic field or composition, in this case by changing (increasing) the Lu concentration. Recently, similar complex experimental studies were performed on $Tm_{1-x}Yb_xB_{12}$ system where a metal-insulator transition (from metallic $TmB_{12}$ to insulating $YbB_{12}$) was observed with the appearance of a QCP near $x_C \approx 0.3$ [10].

In this contribution we present results of heat capacity and electrical resistivity measurements performed on $Ho_{1-x}Lu_xB_{12}$ solid solutions in a wide range of temperatures and in magnetic field. This wide range of experimental conditions allowed us to follow in detail the change of ordering temperature and of other properties with concentration (x).

## 2. Experimental

Experimentally, high-quality single crystals of $HoB_{12}$ and $Ho_{1-x}Lu_xB_{12}$ solid solutions with x = 0.2, 0.5, 0.7 and 0.9 were grown by vertical crucible-free induction zone melting in an inert gas atmosphere. Measurements of heat capacity were performed in wide temperature range of 2-300 K in a magnetic field up to 9 T (B‖<111>) in a PPMS instrument (Quantum Design, US). Electrical resistivity was measured below 3 K down to 50 mK and up to 8 T (B║<111>) in a home-made dilution $^3$He-$^4$He minirefrigerator. Four probe ac - measurement of very small electrical resistance values (≈ 0.1 mΩ) in a non-shielded laboratory was carried out thanks to a special current source with active common mode reduction (Pico Precision, SK).

## 3. Results and discussion

The observed heat capacity data C(T) in zero magnetic field are displayed in Fig. 1. A heat capacity discontinuity, steep increase and the shape of C(T) at $T_N$ = 7.4 for $HoB_{12}$ are typical features of incommensurate amplitude-modulated magnetic structures. With increasing lutetium concentration x (see Fig. 1) or magnetic field *B* (see the example for $Ho_{0.5}Lu_{0.5}B_{12}$ in Fig. 3) the overall heat capacity picture remains similar, but the steep increase of *C(T)* gets reduced in amplitude and the AF phase transitions are shifted to a lower temperatures. As usually, the derivative of heat capacity *C(T)* or of electrical resistivity *ρ(T)* with respect to temperature has been used to define Néel temperature, $T_N$. The resulting phase diagrams $T_N$ vs. *x* (with a linear dependence of $T_N(x)$) and $T_N$ vs. *B* (with a quadratic behavior of $T_N(B)$) are displayed in Fig. 2 and Fig. 4, respectively. The extrapolations of phase boundary lines $T_N$ vs. *x* and $T_N$ vs. *B* down to $T_N$ = 0 K provide then information about critical parameters of concentration $x_C$ and field $B_C$, respectively, of the investigated solid solutions $Ho_{1-x}Lu_xB_{12}$. From received results it follows that AF ordering should disappear at $x_C \approx 0.9$ (see Fig. 2).

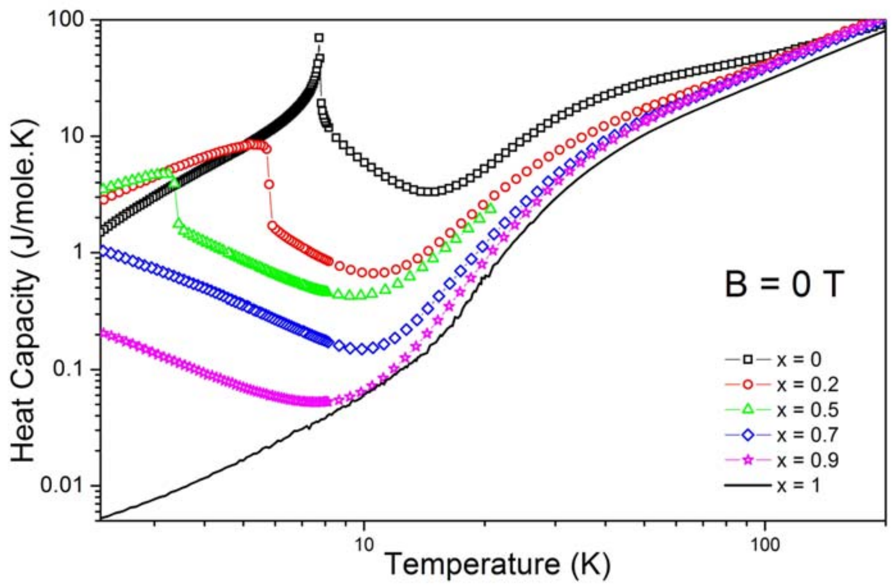



Fig. 1: Temperature dependencies of the heat capacity of dodecaborides $Ho_{1-x}Lu_xB_{12}$ (with x = 0, 0.2, 0.5, 0.7, 0.9 and 1) in zero external magnetic field.

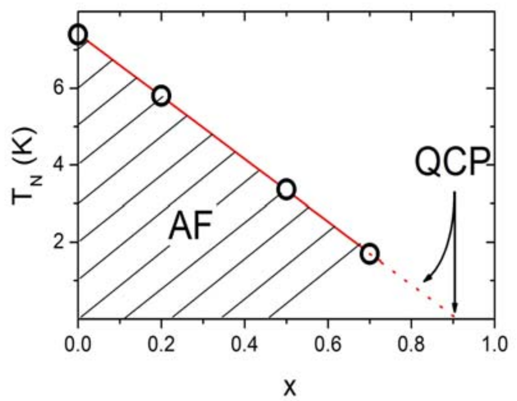



Fig. 2: The magnetic phase diagram of solid solutions $Ho_{1-x}Lu_xB_{12}$ derived from *C(T)* data with a possible QCP at $x \approx 0.9$.

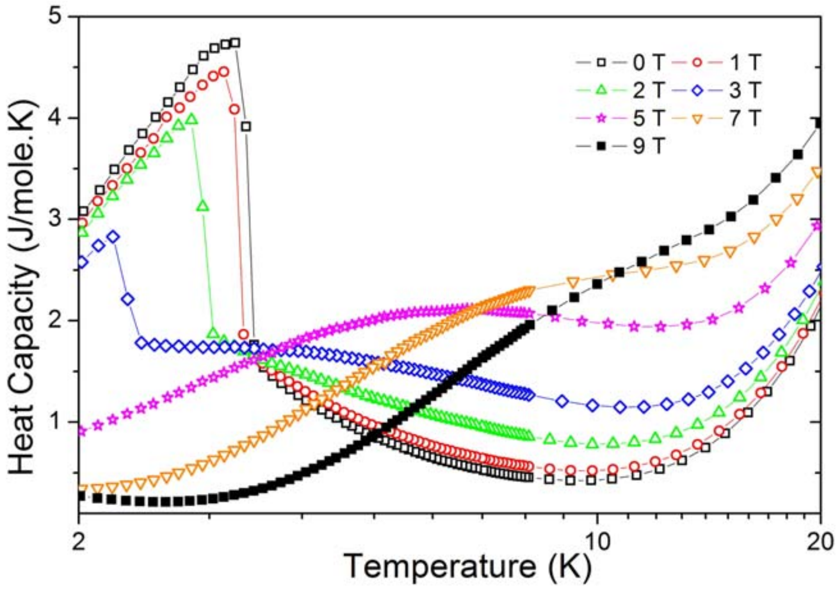



Fig. 3: Temperature dependencies of the heat capacity of $Ho_{0.5}Lu_{0.5}B_{12}$ in magnetic field up to 9 T.

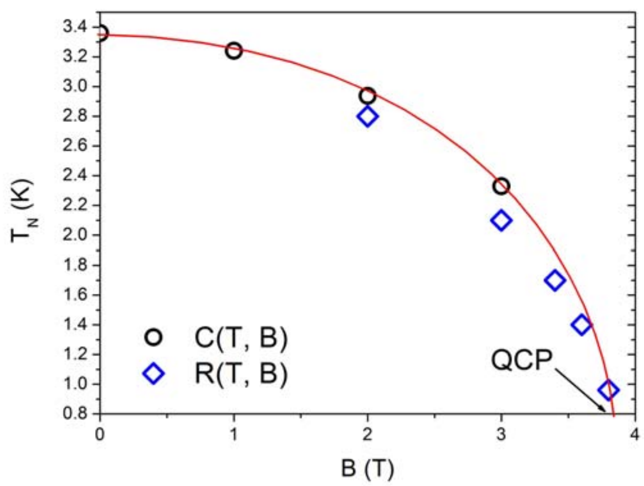



Fig. 4: The phase diagram $T_N$ versus field $B$ of $Ho_{0.5}Lu_{0.5}B_{12}$ derived from heat capacity and magnetoresistance measurements. The obtained dependence points to a QCP at $B_C \approx 3.8$ T. (Note: Magnetoresistance measurements down to 0.5 K and in magnetic field up to 12 T point to a QCP in $HoB_{12}$ at $B_C \approx 8.2$ T [11].)

The temperature dependence of electrical resistivity below 3 K (see Fig. 5) displays the results for $Ho_{1-x}Lu_xB_{12}$ solid solutions with $x = 0.7$, 0.9 and 1 in zero external magnetic field. In the $\rho(T)$ dependence of $Ho_{0.3}Lu_{0.7}B_{12}$ ($x = 0.7$) with $T_N \approx 1.9$ K a typical hump can be seen which reflects the effect of superzone boundaries at transition to the antiferromagnetic state. In $LuB_{12}$ ($x = 1$) at $T_C \approx 0.4$ K a transition into the superconducting state can be observed. However, for $Ho_{0.1}Lu_{0.9}B_{12}$ ($x = 0.9$) there is no evidence of a phase transition (AF or superconducting) down to 50 mK! Furthermore, for this solid solution a $\rho(T) \propto T^2$ dependence was observed, which points to Fermi liquid behavior in this compound, so that a QCP can be expected in the concentration range $0.7 < x_C < 0.9$. In solid solutions which order antiferromagnetically ($x = 0.7$, 0.5, 0.2, 0) the resistivity in the lowest temperature range and in zero magnetic field can be well described by spin wave scattering of conduction electrons $\rho(T) \propto T^b \exp(-\Delta E/k_B T)$, where $\Delta E$ reflects the value of spin wave activation energy. Best fits for these concentrations were received with $b \approx 2$ and with $\Delta E$ decreasing from $\approx 0.25$ meV down to 0.04 meV with x increasing from 0 to 0.7.

The results of magnetoresistance measurements carried out at temperatures far below $T_N$ (at $T$ = 200 mK and in magnetic field up to 9 T) are shown in Fig. 6. A positive magnetoresistance $\Delta\rho/\rho(0T)$ was observed (its amplitude reaches 150 %) for $HoB_{12}$, and the local minimum at $\approx$ 8.2 T can be assigned to critical field $B_C$ of QCP. With increasing x the amplitude of $\Delta\rho/\rho(0T)$ decreases, $B_C$ gradually goes to zero, and for $x = 0.9$ the field dependence of $\Delta\rho/\rho(0T)$ changes to simple quadratic behavior (like for $LuB_{12}$ [7], but with much smaller slope). The received $B_C$ vs. x dependence corresponds well with that obtained from $T_N$ vs. $B$ phase diagrams.

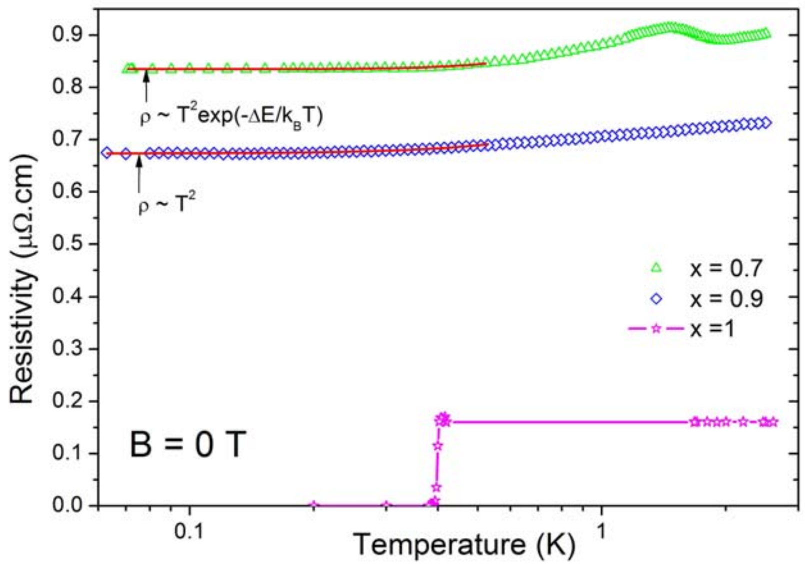



Fig. 5: Temperature dependencies of the electrical resistivity of $Ho_{1-x}Lu_xB_{12}$ (x = 0.7, 0.9 and 1) below 3 K in zero magnetic field. The solid lines represent spin-waves scattering fits (see also text).

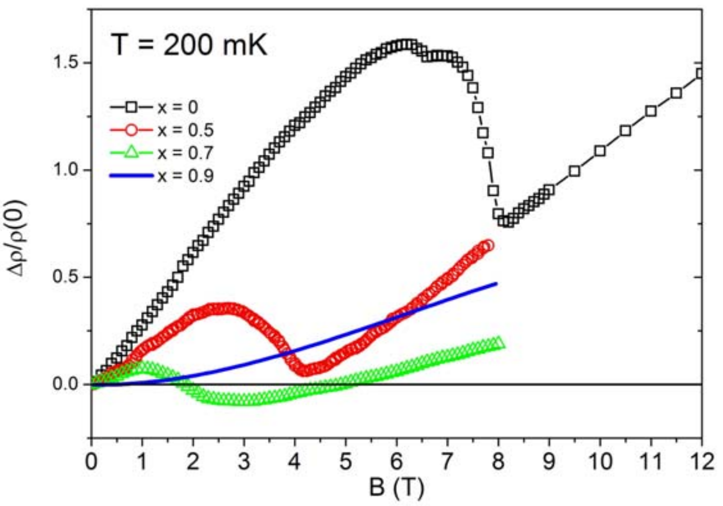



Fig. 6: Field dependencies of magnetoresistance of various $Ho_{1-x}Lu_xB_{12}$ solid solutions at 200 mK (see also text).

Schottky anomalies which can be observed in *C(T)* dependencies of $Ho_{1-x}Lu_xB_{12}$ compounds at about 40 K are quite stable with respect to Lu concentration and to applied magnetic field.

## Conclusions

In this work, we have performed studies of the $Ho_{1-x}Lu_xB_{12}$ system. It was shown that AF order is suppressed to zero temperature, i.e. $T_N \rightarrow 0$, as lutetium concentration increases to $x \approx 0.9$. Phase diagrams of $T_N$ vs. $x$ and $T_N$ vs. $B$ constructed from *C(T)* and *ρ(T)* dependencies point to a possible QCP at $x_C \approx 0.9$, or $B_C(x)$. The observed results / transitions originate probably from the suppression of the dominating RKKY indirect exchange interaction between Ho magnetic ions (mediated via the conduction electrons) and by the suppression of spin fluctuations (and correspondingly spin polarization of the conduction 5 d states) with increasing concentration of Lu nonmagnetic ions and magnetic field, respectively. To shed more light on it, further detailed studies of this system especially at / around the QCP are needed.

## Acknowledgements

This work was supported by the Slovak Scientific Agency (VEGA-0148-10), by the Slovak Research and Development Agency (VVCE 0058), and by the Center of Excellence of the Slovak Academy of Sciences.

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* Corresponding author: flachb@saske.sk