Supplementary Material to the article "Structural transition in dodecaborides according to NMR in LuB_{12}"

1) The **NMR linewidth** in a powder sample is contributed from the homogeneous dipolar broadening, Δ_D, and inhomogeneous broadening associated with the scatter of magnetic, Δ_M, and quadrupole, Δ_Q, shifts. The linewidth components of different nature are non-additive and combine by the operation of convolution. Both Δ_D and Δ_M are the same for all transitions $m \leftrightarrow m-1$, unlike Δ_Q: for the "central" transition ($m = 1/2$) Δ_Q is determined by the scatter of II-order perturbation theory quadrupole shifts ($\Delta_Q = \Delta_{II}$), while for the "satellites" with $m \neq 1/2$, it is related to I order quadrupole shifts, $\Delta_Q = \Delta_I$, whereas $\Delta_I >> \Delta_{II}$. This is the origin of the thirtyfold excess of Δ_B, the broad contribution to the ^{175}Lu linewidth, over the narrow one, Δ_N (see Fig. 2 of the Main paper).

1a) **The NMR dipolar linewidth** caused by the dipolar interactions between spin-*I* nucleus with neighboring spin-*S* nuclei is expressed as [1]

$$\Delta_D = 2(2\ln 2 \Sigma_S M_2^{IS})^{1/2}, \quad \text{(S1)}$$

where the sum is taken over 2nd moments of the NMR line $f(\nu)$,

$$M_2 = \int f(\nu)(\nu - \nu_0)^2 d\nu.$$

For identical ("like") spins, $S = I$,

$$M_2^{II} = \frac{3}{5}\gamma_I^4 h^2 I(I+1) \sum_{I'} r_{II'}^{-6}, \quad \text{(S2a)}$$

and for unlike spins, $S \neq I$,

$$M_2^{IS} = \frac{4}{15}\gamma_I^2 \gamma_S^2 h^2 S(S+1) \sum_{S} r_{IS}^{-6}, \quad \text{(S2b)}$$

where $r_{II'}$, $r_{IS'}$ are internuclear distances and h is the Planck constant. For the 100% ^{11}B-enriched LuB_{12}:

^{175}Lu: spin 7/2, gyromagnetic ratio $^{175}\gamma$ = 4.86 MHz/T, natural abundance 97.4%;

^{176}Lu: spin 7, $^{176}\gamma$ = 3.45 MHz/T, natural abundance 2.6%;

^{11}B: spin 3/2, $^{11}\gamma$ =13.66 MHz/T (100% enriched).

Summation over r^{-6} in Equations (S2) has been taken within 18 Å from (0,0,0) Lu position that included ~60 unit cells, showing satisfactory convergence to 6.3×10^{-4} Å^{-6} for $r_{Lu\text{-}Lu}$ in Eq.(S2a) and to 6.2×10^{-2} Å^{-6} for $r_{Lu\text{-}B}$ in Eq.(S2b), as demonstrated in Fig. S1.

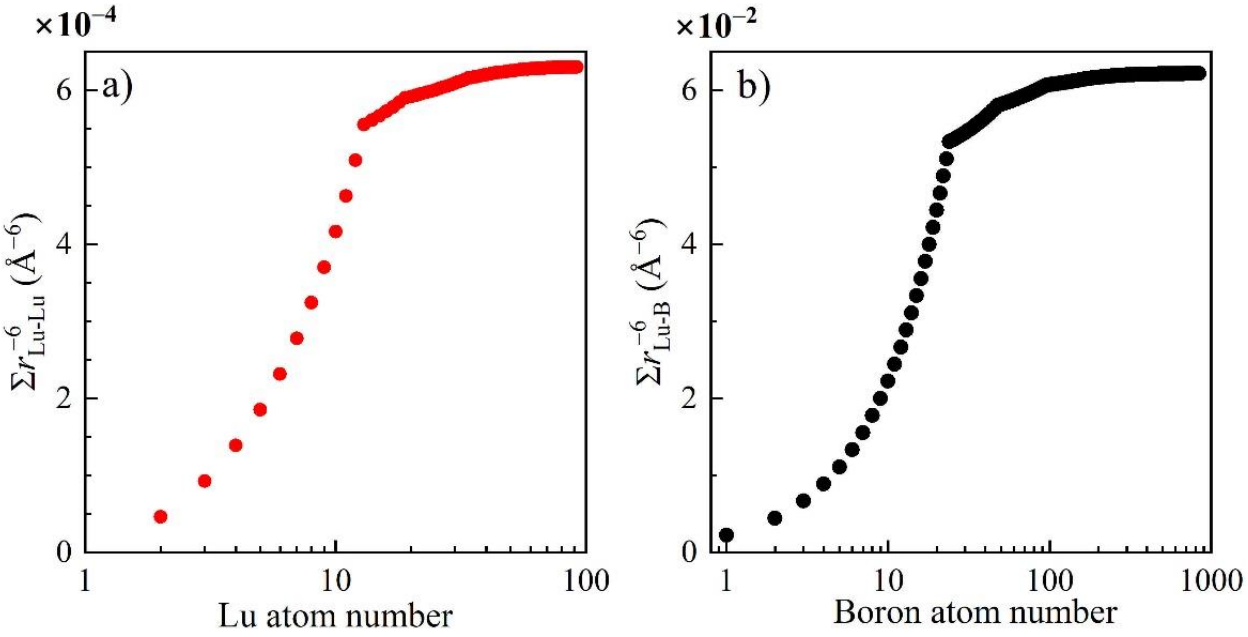

Figure S1. Convergence of the lattice sum Σr^{-6} for internuclear distances Lu-Lu, $r_{\text{Lu-Lu}}$ (a), and Lu-B, $r_{\text{Lu-B}}$ (b).

Using equations (S2) and the sums over r^{-6} shown in Fig. S1, we get:

For dipolar interaction between ^{175}Lu, Eq.(2a): $M_2^{\text{Lu-Lu}}$ = 14 585 Hz^2;

For dipolar interaction between ^{175}Lu and ^{176}Lu, Eq.(2b): $M_2^{\text{Lu-Lu`}}$ = 11 280 Hz^2;

For dipolar interaction between ^{175}Lu and ^{11}B, Eq.(2b): $M_2^{\text{Lu-B}}$ = 1 202 860 Hz^2.

Since the difference between M_2 of the values for "like" ^{175}Lu spins and "unlike" spins ^{176}Lu is minor, whilst the natural abundance of ^{176}Lu is less than 5%, the presence of ^{176}Lu isotope can be neglected without any loss of accuracy, and 100% isotope ^{175}Lu can be accepted: $M_2 = M_{2\,\text{Lu-Lu}} + M_{2\,\text{Lu-B}}$ = 1 217 445 Hz^2. **The full dipole width of the ^{175}Lu NMR line at half maximum, according to Equation (S1), is then Δ_D = 2.6 kHz.**

The value of Δ_D corresponds to the cell parameters of LuB_{12} at room temperature. According to the structural data [2], the cell parameters decrease monotonically upon cooling to 50 K by ~0.04%, which corresponds to an increase in Δ_D by ~0.12%, see Equations (S1), (S2), and change little upon further cooling.

1b) Inhomogeneous broadening of magnetic origin Δ_M, is associated with the scatter or anisotropy of the NMR line shift of **magnetic nature** that is proportional to the absolute value of the shift itself. Fig. S2 depicts the temperature dependence of the narrow-line frequency shift obtained from the fits to the spectrum (see Fig.1 of the Main paper) using Equation (1) of the Main paper, with $K = \nu_N / {}^{175}\gamma B_0 - 1$; ν_{res} = 33709.7 kHz; B_0 = 7.000±0.001 T.

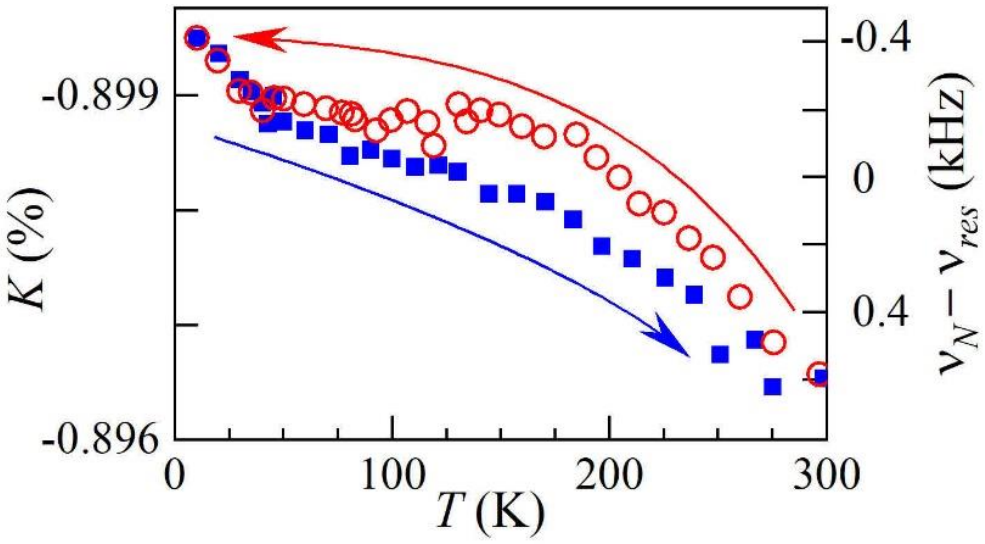

Figure S2. Temperature dependence of the shift of the narrow (*N*) line. The circles (squares) show the data for cooling from 300 K (heating from 10 K)

Fig. S3 presents the narrow line width, Δ_N, as a function of its shift, ν_N, measured upon heating. A noticeable change in the behavior of $\Delta_N(\nu_N)$ is observed at 50 K. The **linear** dependence of Δ_N on the lineshift **at *T*<50K assumes the magnetic nature of the temperature-dependent linewidth** Δ_N.

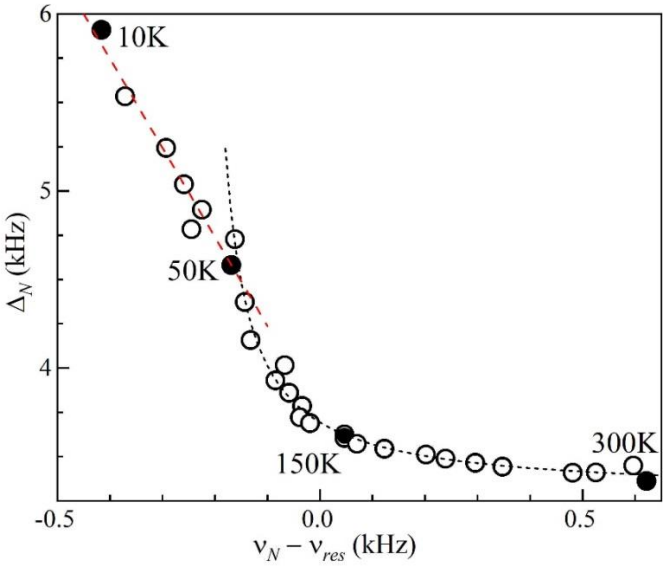

Figure S3. The narrow-line width, Δ_N, *vs* its shift, ν_N. Solid symbols are temperature marks.

2) The spin-lattice relaxation of ^{175}Lu.

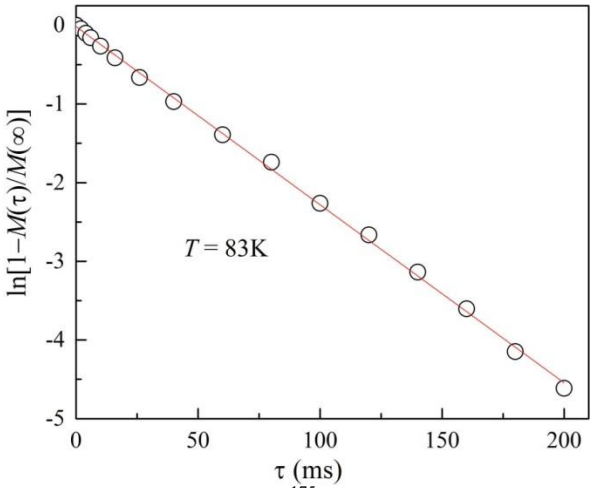

Figure S4a. An example of ^{175}Lu relaxation transient for T_1 at 83K.

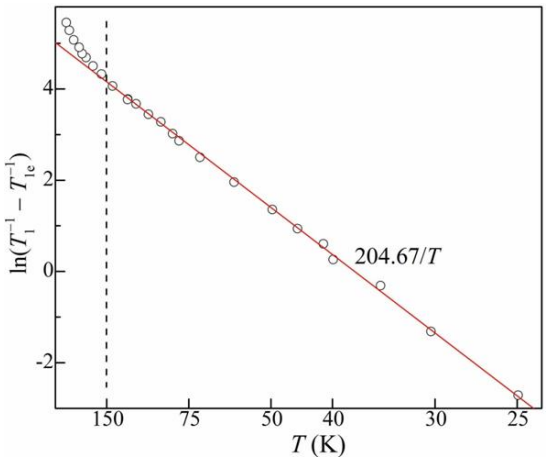

Figure S4b. Logarithm of the quadrupolar contributon to ^{175}Lu spin-lattice relaxation, $1/T_{1Q} = 1/T_1 - 1/T_{1e}$ as a function of the inverse temperature, demonstrating the gap-like character of the temperature dependence of $1/T_{1Q}$ at T<150K. Here, $1/T_{1e}$=0.037T is the electronic contribution to the relaxation that dominates at T<25K.

3) The Korringa relation ties the electronic contribution of the nuclear spin-lattice relaxation rate $1/T_{1e}$ and the spin part of the NMR line shift K_{spin} for the system of non-interacting electrons:

$$T_{1e}^{-1} = \frac{4\pi k_B}{\hbar}\left(\frac{\gamma_n \hbar}{g\mu_B}\right)^2 K_{spin}^2 T, \qquad \text{(S3)}$$

where k_B is the Boltzmann constant, ħ is the Planck constant, g is the Landé factor, μ_B is the Bohr magneton, K_{spin} is the spin part of the line shift (the Knight shift) due to the spin susceptibility of the conducting electron system. The NMR shift of magnetic origin $K = \sigma + K_{spin}$, where σ is the chemical shift. In semiconducting LuSb at room temperature, $K_{LuSb} = -0.841\%$ [3]; here $K_{spin} = 0$ because there is no contribution from conduction electrons, so that $\sigma = K_{LuSb}$. LuB_{12} belongs to the same space group $Fm\bar{3}m$ as LuSb, but with the centers of B_{12} cuboctahedra in the positions of the antimony atoms. Therefore, it is reasonable to assume that the chemical shift of lutetium, σ, is the same in both compounds. Accordingly, for LuB_{12} $K_{spin} = K - \sigma = -0.0571 \pm 0.0015\%$, where K is the shift value in Fig. S2. The error in determining K_{spin} is due to the fact that the temperature change in K can be associated both with σ and K_{spin}.

1. A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, New York, 1961.
2. A. P. Dudka, E. S. Smirnova, I. A. Verin, N. B. Bolotina, Cryst. Reports **62**, 651 (2017).
3. A. H. Reddoch, G. J. Ritter, Phys. Rev. **126**, 1493 (1962).