$EuNi_2P_4$, the first magnetic unconventional clathrate prepared via mechanochemically assisted route

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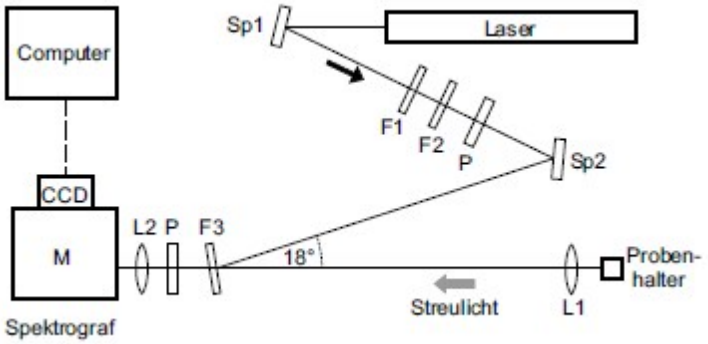
RAMAN SETUP



The Raman spectrometer is a homemade setup. It is equipped with a HeNe laser providing 35 mW at 632 nm. Signal detection is accomplished with a CCD camera attached to a grating spectrograph with 350 mm focal length and 1800/mm grating. The CCD-chip has a 1024x256 pixel active area and was operated in full vertical binning mode. Under these conditions and for the wavelength range dictated by the laser the CCD chip cover a spectral range of roughly 50 nm with 1024 data points. The laser is focused to the sample by a microscope objective (20x) (L1) and the signal is collected by the same objective in backward direction and finally focused by a lens (L2) to the entrance slit of the spectrograph. The collinear arrangement of laser beam and the spectrograph's optical axis is accomplished by a notch filter (F3) which at an incident angle of 9° reflects a spectral range of +/- 130 cm^{-1} centered to the laser frequency and transmits all other frequencies. The CCD camera is connected to a PC where spectra are digitally stored.

Two mirrors (Sp1, Sp2) for guiding the laser two filters (F1, F2) serve to eliminate other than the 632 nm laser line. (We have not been using a polarizer neither in the laser beam nor before the spectrograph).

The Raman shift was calibrated by means of an Ar-Ne lamp using the corresponding atomic lines as provided by NIST.

Table S1. Details of synchrotron powder diffraction experiments for $EuNi_2P_4$ at different temperatures.

Phase	$EuNi_2P_4$					
Temperature in K	10	50	100	150	250	273
λ in Å	0.35456					
2θ range in deg	1 – 40					
d-spacing range in Å	0.5 – 20.3					
Space group	*Fddd (No. 70, origin choice 1)*					
Z	*8*					
Density in g/cm^3	5.630	5.628	5.626	5.621	5.598	5.594
Cell parameters						
a in Å	5.1737(1)	5.1742(1)	5.1749(1)	5.1762(1)	5.1841(1)	5.1852(1)
b in Å	9.4518(1)	9.4534(1)	9.4561(1)	9.4602(1)	9.4812(1)	9.4835(1)
c in Å	18.9754(2)	18.9758(2)	18.9752(2)	18.9765(2)	18.9864(2)	18.9894(2)
V inÅ^3	927.93(2)	928.18(2)	928.54(2)	929.24(2)	932.20(2)	933.79(2)
Data points	26000	26000	26000	26000	26000	26000
Overall parameters	31	36	30	33	32	31
Reflections	881	881	881	884	887	887
Structural parameters	11	11	11	11	11	11
R values						
R_F	2.55	2.71	3.06	4.35	3.86	3.20
R_P	14.22	13.90	13.54	12.53	9.63	10.35
R_{wP}	18.80	18.35	18.10	16.90	13.92	14.80
χ^2	1.62	1.69	1.63	1.76	2.56	2.53

Table S2. Refined atomic coordinates and atomic displacement parameters in the crystal structure of $EuNi_2P_4$ at different temperatures.

Atom	Site	10K	50K	100K	150	250	273
Eu	8*b* (0; 0; 0)						
	U_{eq}	0.0029(1)	0.0039(2)	0.0058(2)	0.0111(2)	0.0146(2)	0.0144(2)
	U_{11}	0.0013(2)	0.0018(2)	0.0034(3)	0.0055(3)	0.0098(3)	0.0104(3)
	U_{22}	0.0040(3)	0.0045(3)	0.0057(3)	0.0075(3)	0.0106(3)	0.0110(3)
	U_{33}	0.0036(3)	0.0055(3)	0.0082(2)	0.0132(3)	0.0226(4)	0.0240(3)
Ni	16*g* (0; 0, *z*)						
	z	0.11987(5)	0.11983(5)	0.11987(5)	0.12008(5)	0.11993(5)	0.11979(5)
	U_{iso}	0.0050(2)	0.0050(2)	0.0058(2)	0.0071(2)	0.0090(2)	0.0093(2)
P	32*h* (*x*; *y*; *z*)						
	x	0.3116(3)	0.3121(3)	0.3118(3)	0.3113(3)	0.3115(2)	0.3117(3)
	y	0.0568(1)	0.0572(1)	0.0571(1)	0.0569(1)	0.0570(1)	0.0570(1)
	z	0.19380(8)	0.19371(8)	0.19377(8)	0.19417(7)	0.19397(7)	0.19380(7)
	U_{iso}	0.0049(3)	0.0049(3)	0.0055(2)	0.0072(3)	0.094(3)	0.0096(3)

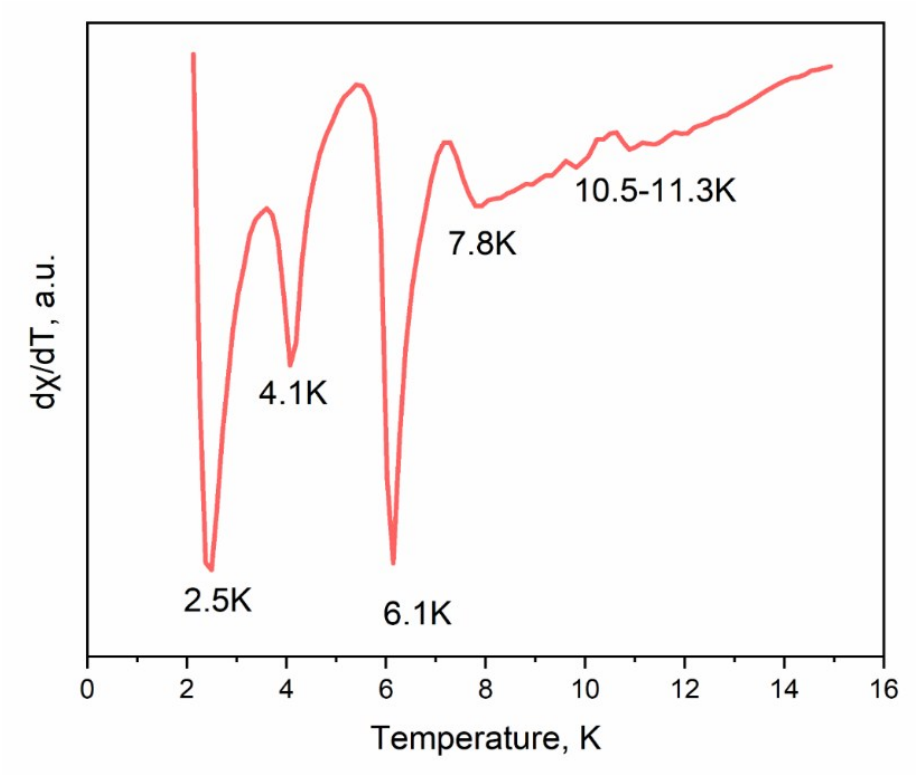


Figure S1. The first derivative of the 0.005 T magnetic susceptibility curve for $EuNi_2P_4$. The anomalies are outlined.

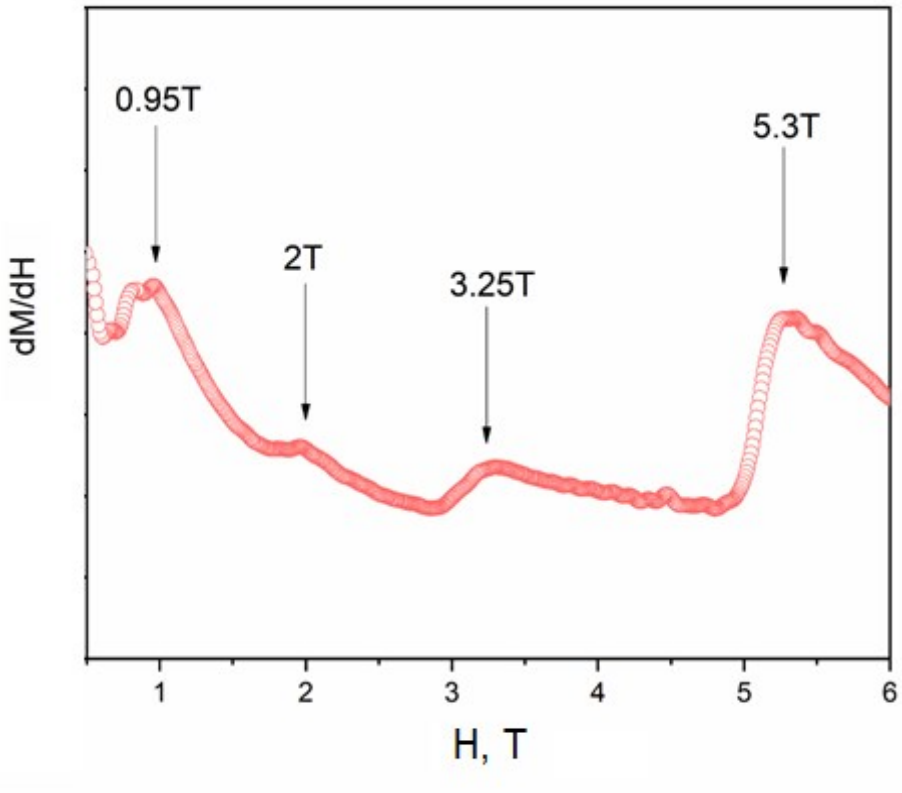


Figure S2. The first derivative of the magnetization curve taken at 1.8 K for $EuNi_2P_4$. The anomalies are outlined.

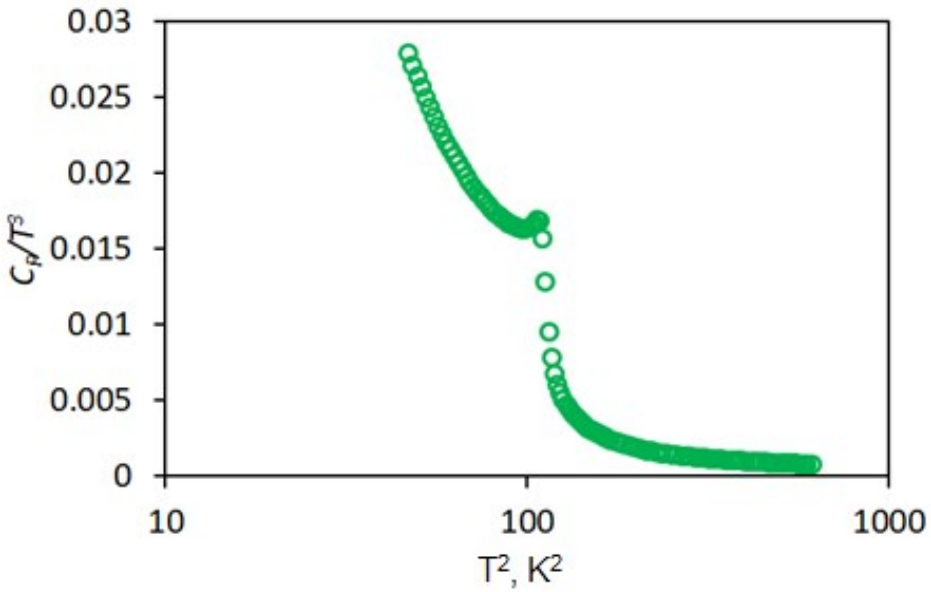


Figure S3. C_P/T^3 *vs* T^2 plot for $EuNi_2P_4$ intended to recover the contribution of the Einstein modes to heat capacity.

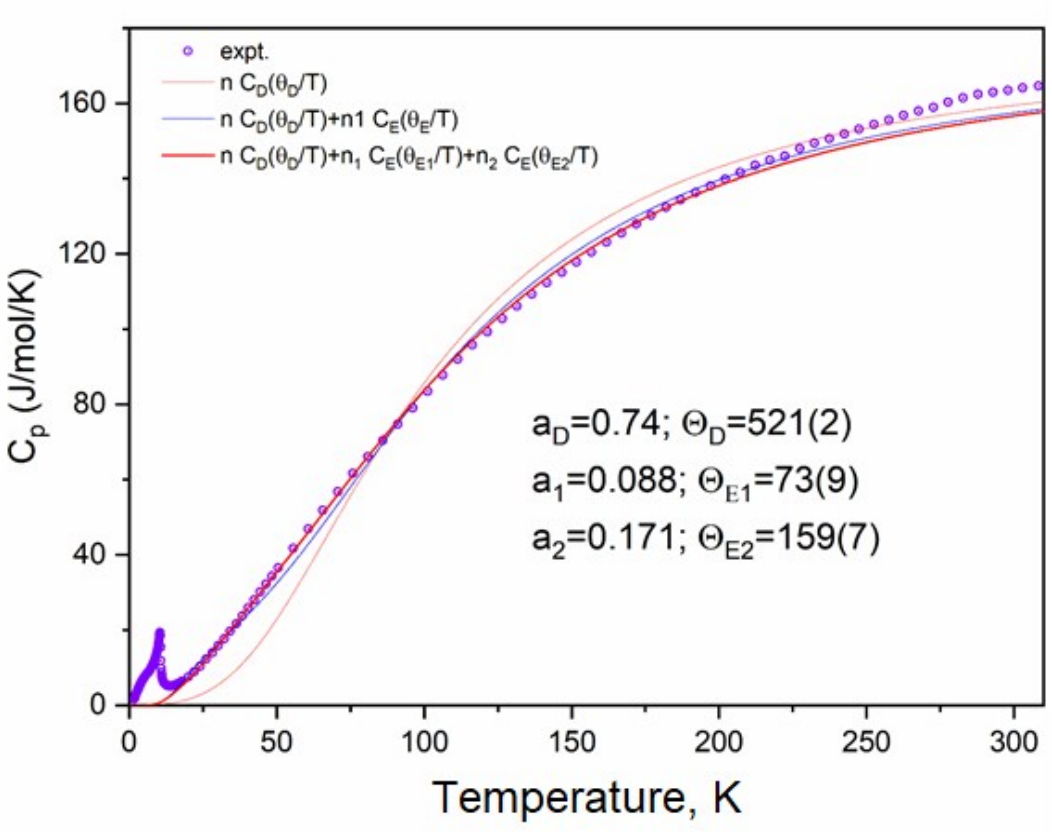


Figure S4. Heat capacity vs temperature plot and attempts to fit it with the Debye function, combination of the Debye function and one Einstein, combination of the Debye function and two Einstein. Fitting parameters for the last case are provided on the plot.

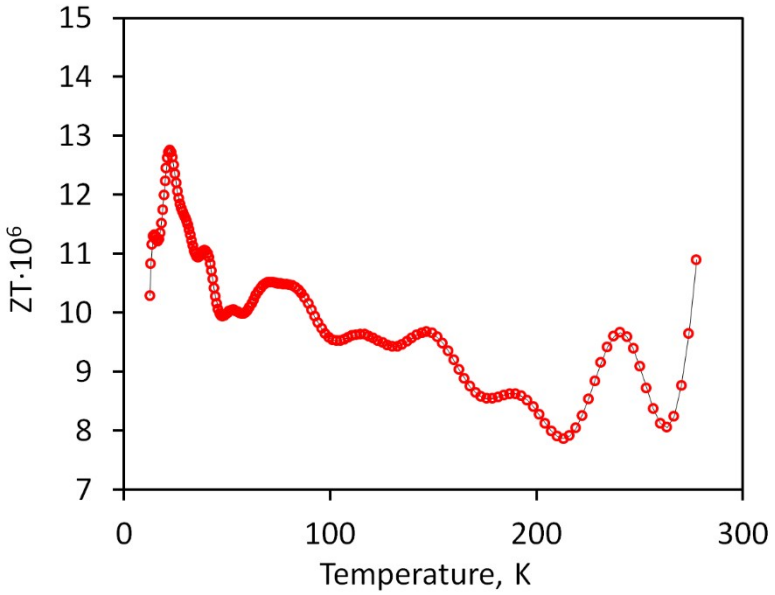


Figure S5. ZT (thermoelectric figure-of-merit) *vs* temperature plot for $EuNi_2P_4$.

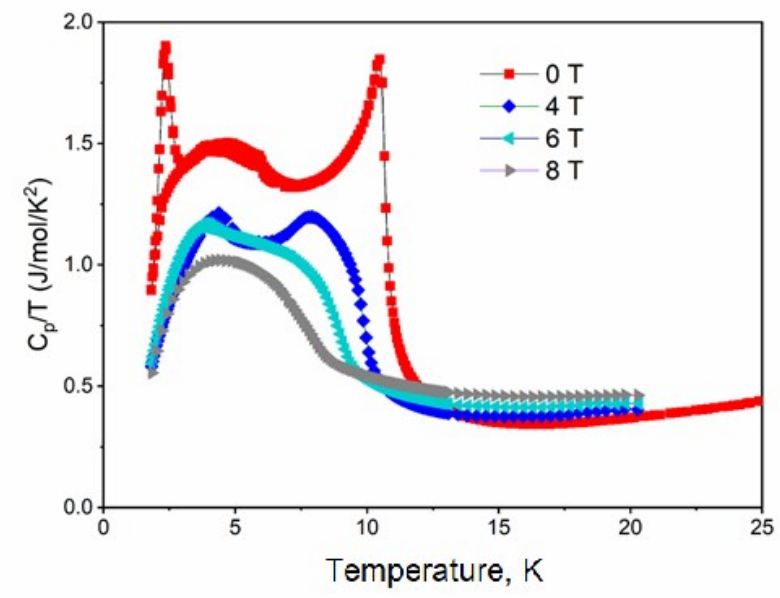


Figure S6. C_P/T *vs* T plot for $EuNi_2P_4$ in high fields.

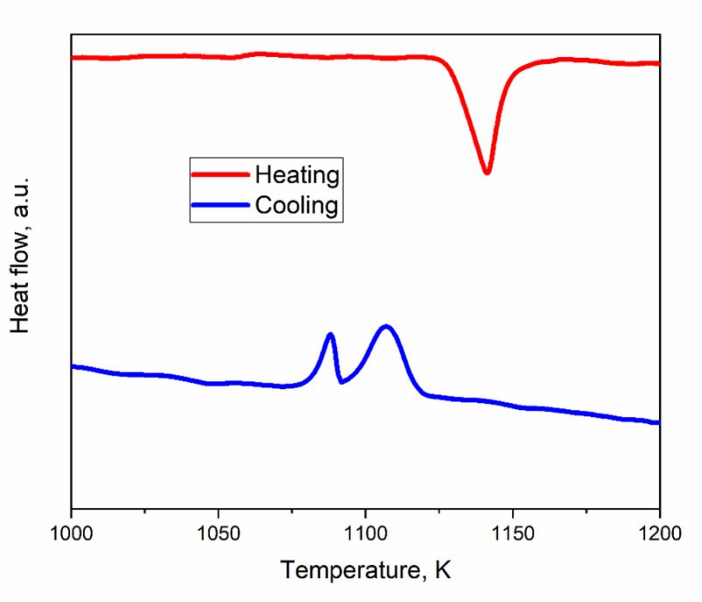


Figure S7. Differential thermal analysis curve for $EuNi_2P_4$.

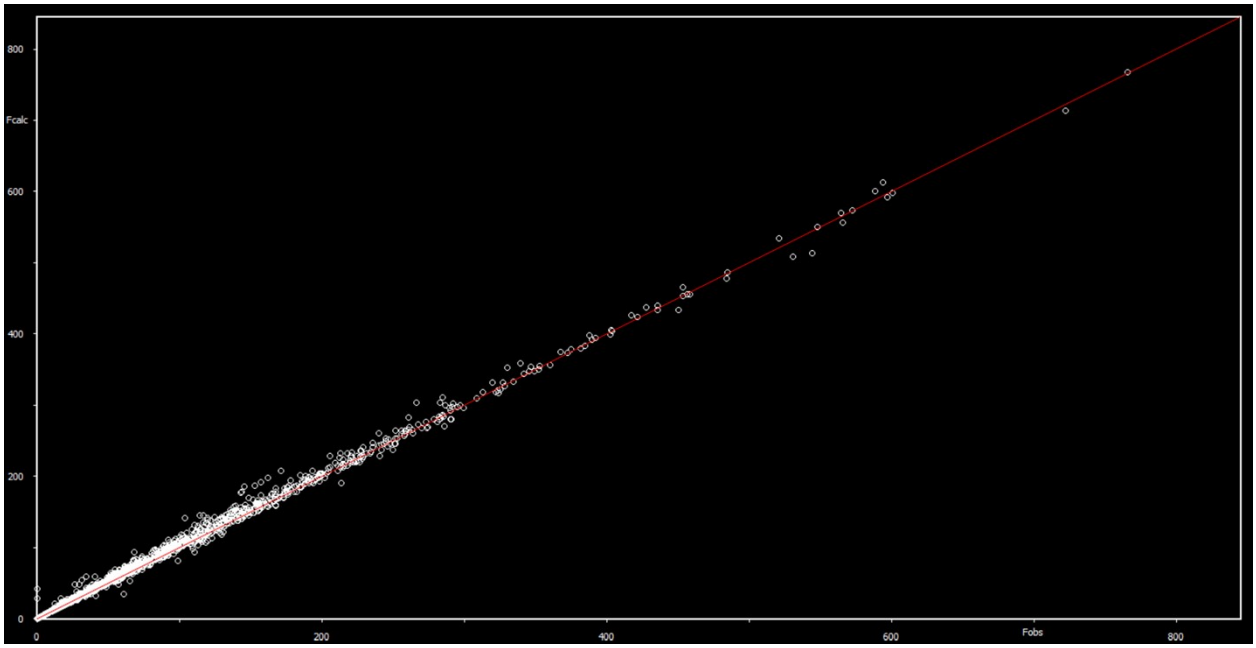


Figure S8. F_{obs} vs F_{cal} plot for $EuNi_2P_4$.

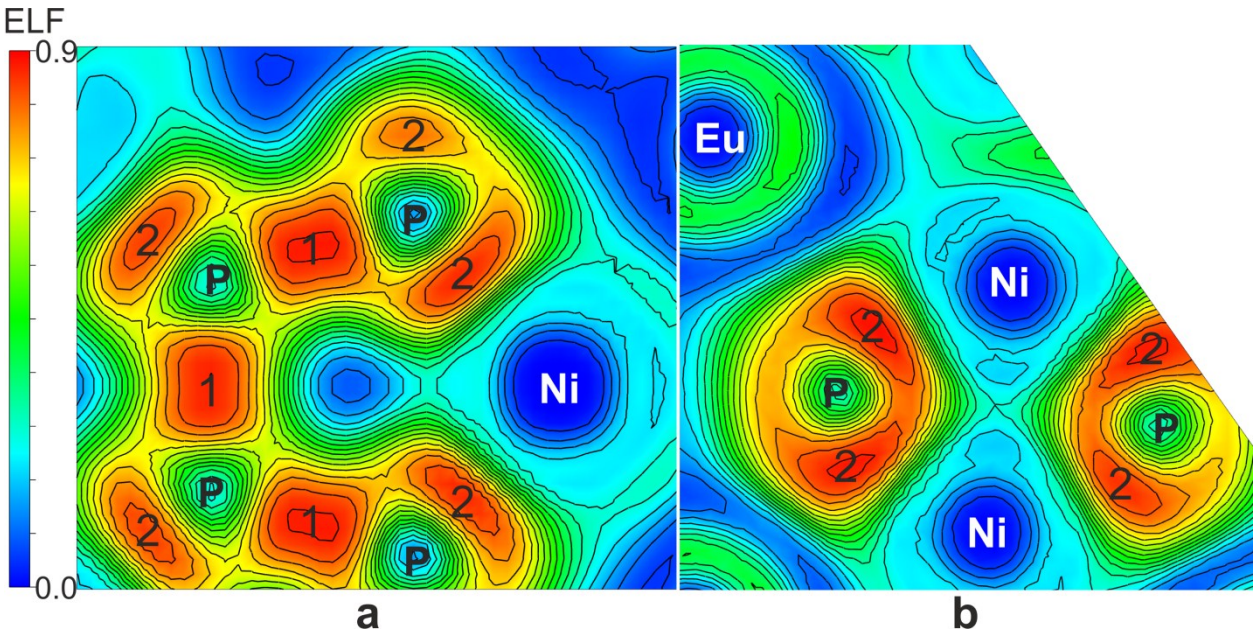


Figure S9. ELF sections passing through a) P-P and P-Ni bonds, and b) P-Ni and P-Ni bonds. Localization domains corresponding to P-P bonds are labelled as 1, and P-Ni bonds as 2.

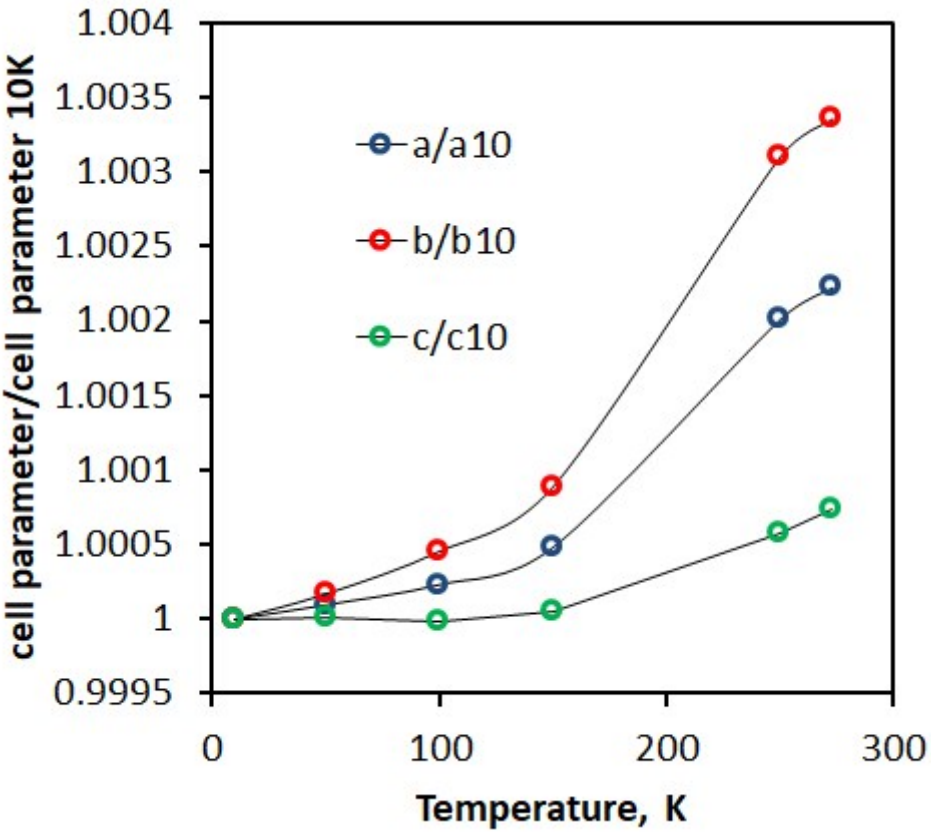


Figure S10. Temperature dependence of *a*, *b* and *c* unit cell parameters.