Electronic Supplementary Information

High-pressure phase of Na_2CuF_4 with eight-coordinated Cu^{2+} – a low-pressure analogue of Mg_2SiO_4

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Synthesis of Na_2CuF_4

All manipulations were performed under anhydrous conditions. Non-volatile substances were handled in a MBraun glove box in an argon atmosphere in which the amount of water did not exceed 0.5 ppm. Volatile compounds, such as anhydrous HF and F_2, were handled on a vacuum line constructed from nickel and PTFE (polytetrafluoroethylene). The vessel, used for the synthesis of CuF_2 at room temperature consisted of a tube (i.d. 16 mm, o.d. 19 mm) made of tetrafluoroethylene-hexafluoropropylene block-copolymer (FEP; Polytetra GmbH, Germany). It was heat-sealed at one end and fitted with a PTFE valve at the other end. Commercially available NaF (Merck, 99 %) was treated with elemental fluorine at 250 °C before use. CuF_2 was prepared by fluorination of $CuCl_2$ (Aldrich, 99.9995 %) with elemental fluorine in anhydrous liquid hydrogen fluoride at room temperature. The resulting CuF_2 was additionally treated with 3 bar elemental fluorine at 260 °C for 24 hours in a nickel autoclave.

The synthesis of Na_2CuF_4 is based on the solid-state reaction between 181 mg (4.32 mmol) NaF and 219 mg (2.16 mmol) CuF_2. The starting mixture was ground on an agate mortar, placed in a Pt-boat covered with a Pt-lid and sealed in a nickel reactor (130 ml) under a dry argon atmosphere. The reactor was evacuated. Under these conditions, the mixture of 2NaF / CuF_2 was heated to about 520 °C. After 23 hours of heating, the reactor was cooled to room temperature and the mixture was ground again. The synthesis procedure was repeated. After a further annealing at 525 °C for 47 hours, the colorless sample was obtained. Its purity was verified by x-ray powder diffraction (see Fig. S1) showing no impurities present.

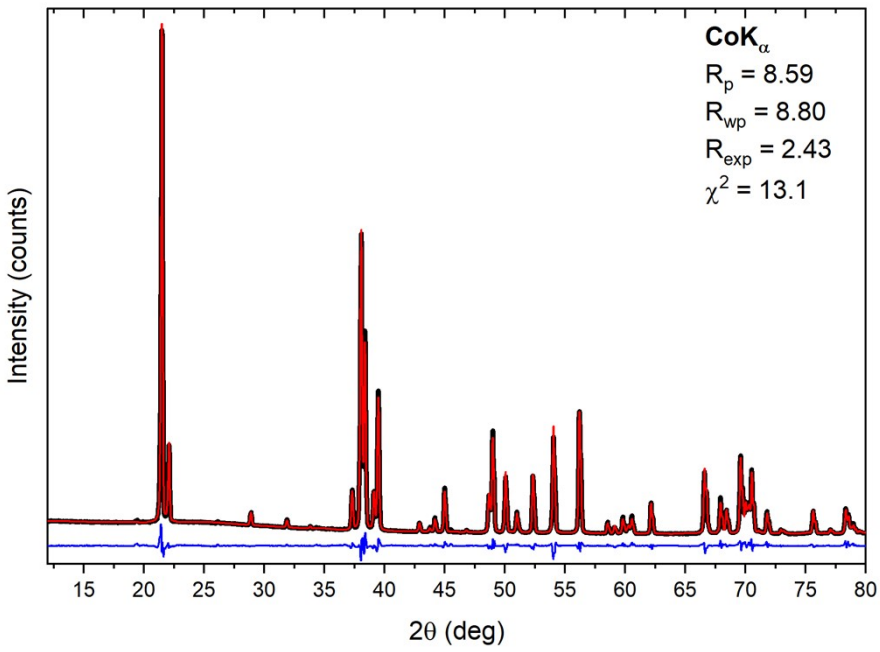

FIG. S1 Powder x-ray diffraction patterns (black lines) of Na_2CuF_4 synthesized as described in the Methods section of the manuscript. Red lines depict a Rietveld refinement model which included the ambient-pressure *$P2_1/c$ (α)* structure of Na_2CuF_4; [1] blue lines depict difference between model and experiment. The pattern was obtained from a powder enclosed in a 0.5 mm quartz capillary (Hingelberg, glass no 50) using Panalytical diffractometer X'Pert Pro with CoKα radiation (0.026° 2θ step / 1316 seconds per step). Rietveld refinement was conducted with FullProf programme.

Raman measurements

Raman spectra were collected at room temperature using an Alpha300M+ confocal microscope (Witec Gmbh). A 532 nm laser line was delivered to the microscope via a single-mode optical fiber, with the laser power at the sample not exceeding 25 mW. The Raman signal was collected through a 50× long working distance objective (NA = 0.40) and transmitted through a photonic-crystal fiber to a lens-based spectrometer (Witec UHTS 300, f/4 aperture, focal length 300 mm) equipped with a back-illuminated Andor iDUS 401 detector, which was thermoelectrically cooled to -60 °C. The spectra were acquired using a 1800 mm^{-1} grating, resulting in a spectral resolution of 1.2 cm^{-1}. The typical acquisition times ranged from 5 to 20 seconds with 15 to 30 accumulations. Additional area scans (120 µm x 120 µm in 2 µm steps) were performed at selected pressures using a 900 mm^{-1} grating (spectral resolution of 5 cm^{-1}) in order validate sample homogeneity and pressure gradients within the DAC. The collected spectra were post-processed using the Project FIVE software (Witec Gmbh) be performing background subtraction, cosmic-ray removal, and smoothing. The positions of Raman bands were determined using the Fityk 1.3.1 software by fitting the observed bands with pseudo-Voigt profiles.

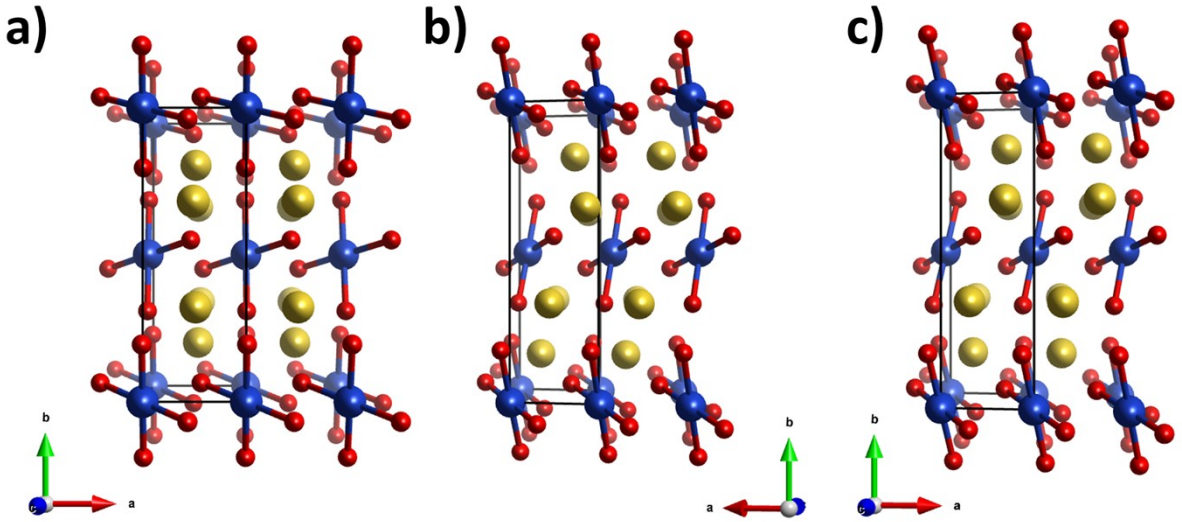

FIG. S2 Comparison of the structure of: (a) *P2₁/c (α)*, (b) *P2₁*, and (c) *P2₁/c (β)*. Yellow/blue/red balls denote Na/Cu/F atoms.

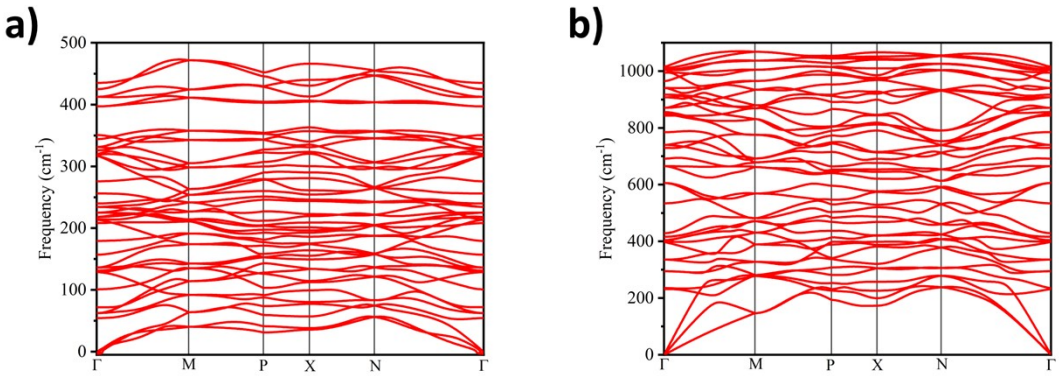

FIG. S3 Phonon dispersion curves calculated for the $I\bar{4}2d$ structure of Na_2CuF_4 at: (a) 1 atm and (b) 300 GPa.

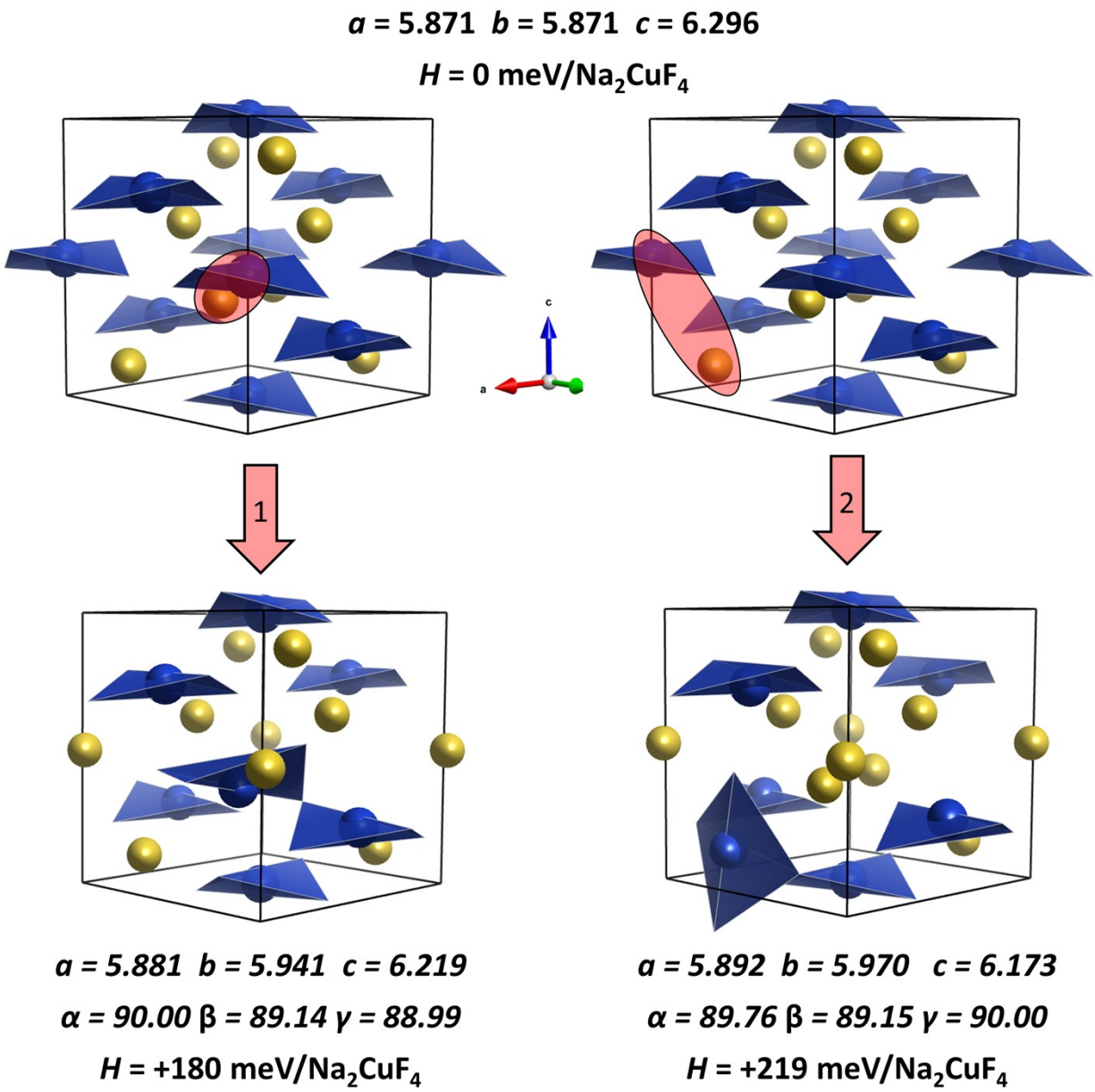

FIG. S4 Schematic depiction of the two irreproducible Na_2CuF_4 structures of *P1* symmetry obtained through a single Na/Cu exchange in the conventional cell of $I\bar{4}2d$. The lattice parameters (in Å) and cell angles (in °) are given for the structures after geometry optimization at 50 GPa, as well as their enthalpies relative to the parent tetragonal structure. Fluorine atoms are omitted for clarity.

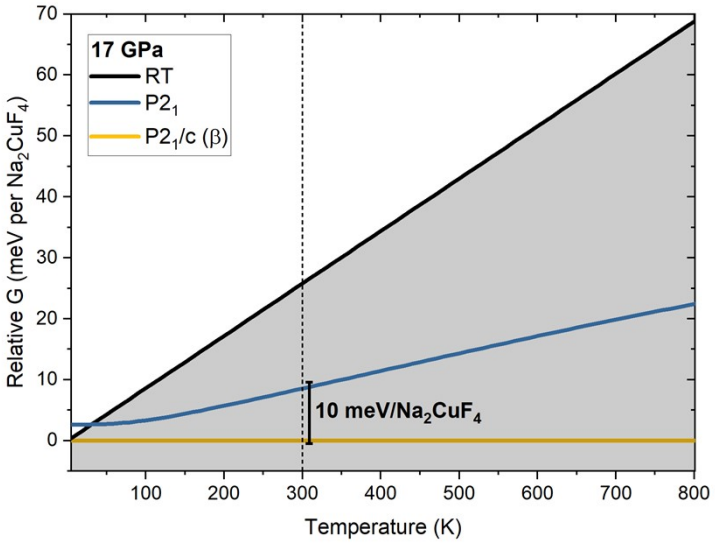

FIG. S5 Gibbs free energy of *P2₁* relative to that of *P2₁/c (β)* calculated at 17 GPa compared to thermal energy (*R*·*T*).

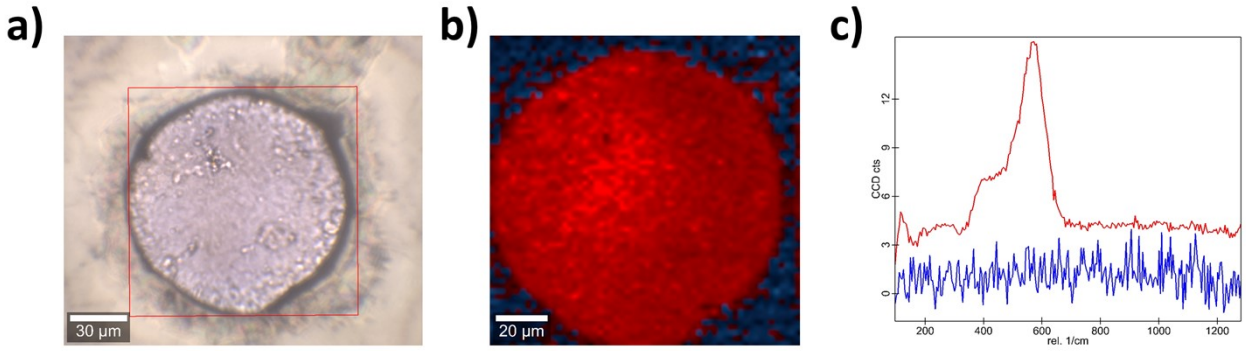

FIG. S6 (a) White-light photograph of a Na_2CuF_4 sample enclosed in a DAC at 42 GPa – red lines denote the boundaries of the Raman areas scan conducted at this pressure; (b) colour map marking areas for which respective spectra, given in (c) with the same colour-coding, are observed.

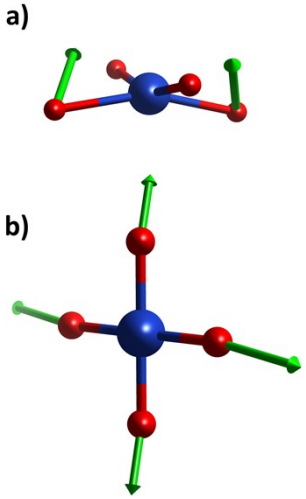

FIG. S7 Comparison of the movement of atoms in the first coordination sphere of Cu^{2+} in the most intense Raman-bands of: (a) $I\bar{4}2d$ at 40 GPa ($4A_1$ mode at 567 cm^{-1}) and (b) *P2₁/c (β)* at 40 GPa ($9A_g$ mode at 625 cm^{-1}).

Table S1. Calculated structural details of Na_2CuF_4 phases

Phase	Pressure	Lattice parameters	Atomic coordinates
P2$_1$/c (α)	1 atm	*a* = 3.238 Å *b* = 9.279 Å *c* = 5.593 Å *β* = 92.15°	Cu 2 a 0.00000 0.00000 0.00000 Na 4 e 0.51232 0.68184 -0.07953 F 4 e 0.56899 -0.04953 0.76931 F 4 e 0.00746 0.68879 0.62548
P2$_1$	10 GPa	*a* = 2.975 Å *b* = 9.752 Å *c* = 5.139 Å *β* =103.15°	Cu 2 a 0.41221 0.49990 0.75322 Na 2 a 0.71288 0.35498 0.28450 Na 2 a 0.11699 0.67221 0.22975 F 2 a 0.26785 0.05474 0.51121 F 2 a -0.08816 -0.05599 -0.0139 F 2 a 0.33335 0.32512 0.60203 F 2 a 0.49802 0.67011 -0.0894
P2$_1$/c (β)	10 GPa	*a* = 2.949 Å *b* = 9.705 Å *c* = 5.152 Å *β* = 101.13°	Cu 2 a 0.00000 0.00000 0.00000 Na 4 e 0.68614 0.15939 0.46918 F 4 e 0.31868 0.44949 0.23128 F 4 e 0.10264 0.17493 0.14569
$I\bar{4}2d$	50 GPa	*a* = *b* = 5.871 Å *c* = 6.296 Å	Cu 4 a 0.00000 0.00000 0.00000 Na 8 d 0.60622 0.25000 0.12500 F 16 e 0.56917 0.19685 0.44990
P1 **(Cu/Na interchange 1)**	50 GPa	*a* = 5.881 Å *b* = 5.941 Å *c* = 6.219 Å *α* = 90.00° *β* = 89.14° *γ* = 88.99°	Cu 1 a 0.23429 0.35869 0.38699 Cu 1 a 0.50525 0.00245 0.25641 Cu 1 a 0.50227 0.50837 -0.00453 Cu 1 a -0.00159 0.50385 0.75193 Na 1 a 0.10916 0.75035 0.12084 Na 1 a 0.89052 0.24805 0.11663 Na 1 a 0.74833 0.89832 0.87078 Na 1 a 0.25290 0.10667 0.87502 Na 1 a 0.38151 0.75375 0.61505 Na 1 a 0.62096 0.24728 0.63191 Na 1 a -0.00214 -0.01850 0.49625 Na 1 a 0.75523 0.61977 0.37820 F 1 a -0.07005 0.31159 0.43203 F 1 a 0.08969 0.65758 0.43969 F 1 a 0.31151 0.08875 0.55267

			F 1 a 0.67285 -0.07413 0.55172 F 1 a 0.54290 0.32276 0.31729 F 1 a 0.43858 0.70181 0.28902 F 1 a 0.19938 0.06193 0.20062 F 1 a 0.80793 -0.06531 0.19776 F 1 a 0.42971 0.80648 -0.05961 F 1 a 0.56881 0.20303 -0.03619 F 1 a 0.80693 0.57008 0.05167 F 1 a 0.20122 0.42699 0.07044 F 1 a 0.06627 0.80341 0.79343 F 1 a -0.06325 0.20234 0.79181 F 1 a 0.69439 0.56714 0.70107 F 1 a 0.30645 0.43649 0.71108
P1 **(Cu/Na interchange 2)**	50 GPa	a = 5.892 Å b = 5.970 Å c = 6.173 Å α = 89.76° β = 89.15° γ = 90.00°	Cu 1 a 0.75054 0.10652 0.87610 Cu 1 a -0.00013 0.50426 0.72909 Cu 1 a 0.50228 0.50272 0.00653 Cu 1 a 0.49340 -0.00705 0.26673 Na 1 a 0.00518 -0.00510 0.49266 Na 1 a 0.25225 0.89075 0.86807 Na 1 a 0.89496 0.74626 0.12587 Na 1 a 0.11070 0.25353 0.13513 Na 1 a 0.74935 0.38203 0.38082 Na 1 a 0.24463 0.61764 0.37490 Na 1 a 0.37760 0.25337 0.62079 Na 1 a 0.61802 0.75211 0.61975 F 1 a 0.32972 -0.07106 0.54675 F 1 a 0.69195 0.08447 0.58217 F 1 a 0.07405 0.31945 0.45684 F 1 a -0.08166 0.67883 0.44504 F 1 a 0.30479 0.56998 0.69952 F 1 a 0.69341 0.43984 0.70766 F 1 a 0.05384 0.18886 0.81505 F 1 a -0.06690 0.80712 0.80092 F 1 a 0.80443 0.43139 0.05317 F 1 a 0.19994 0.56509 0.04887 F 1 a 0.57016 0.80853 -0.05335 F 1 a 0.44506 0.19082 -0.06169 F 1 a 0.79354 0.06863 0.18342 F 1 a 0.18876 -0.06772 0.19253 F 1 a 0.56487 0.69204 0.29418 F 1 a 0.43524 0.29669 0.29247

Table S2. Position of Raman bands (in cm^{-1}) of the high-pressure phases of Na_2CuF_4 obtained in a DAC experiment and DFT modelling at various pressures together with the assignment of their symmetry.

***P2₁/c* (1 atm)**			***P2₁* (15 GPa)**			***P2₁/c (β)* (25 GPa)**			$I\bar{4}2d$ **(40 GPa)**		
Mode	**Exp.**	**Th.**	**Mode**	**Exp.**	**Th.**	**Mode**	**Exp.**	**Th.**	**Mode**	**Exp.**	**Th.**
$1A_g$	97	93	*3A*	110	118	$1A_g$	119	121	$1B_1$	114	109
			4A	145	147				$1B_2$	135	152
			2B	153	152	$1B_g$	166	176			
$4A_g$	179	180	*5A*	188	179	$2B_g$	180	205	1E	185	176
$5A_g$	197	198	*5B*	201	194						
$5B_g$	219	218	*7A*	228	230				$2A_2$	234	262
			7B	242	242	$4A_g$	265	255	$2B_1$	284	282
			9A, 9B	281	270, 277						
			10B	305	300	$4B_g$	303	292			
$7B_g$	310	319	*13A*	339	342	$5B_g$	323	321			
$8A_g$	321	323	*15A*	370	369	$6A_g$	361	351	$2A_1$	388	373
			16A	383	388						
$8B_g$	368	365	*15B*	400	404	$7A_g$	449	445	$3B_1$	416	471
			17A	434	432	$8B_g$	481	503			
$9A_g$	457	447	*19A*	520	520	$8A_g$	516	518			
$9B_g$	475	461	*18B*	536	543	$9A_g$	593	572	$5B_2$	538	513
			20A	558	563	$8B_g$	611	586	$4A_1$	577	567

References

[1] D. Babel, *Untersuchungen an Ternaren Fluoriden. III) Die Struktur Des Na_2CuF_4*, Zeitschrift Fur Anorg. Und Allg. Chemie **336**, 200 (1965).