Frustrated magnet for adiabatic demagnetization cooling to milli-Kelvin temperatures

Yoshifumi Tokiwa1,2✉, Sebastian Bachus1, Kavita Kavita1, Anton Jesche1, Alexander A. Tsirlin1 & Philipp Gegenwart1

Generation of very low temperatures has been crucially important for applications and fundamental research, as low-temperature quantum coherence enables operation of quantum computers and formation of exotic quantum states, such as superfluidity and superconductivity. One of the major techniques to reach milli-Kelvin temperatures is adiabatic demagnetization refrigeration. This method uses almost non-interacting magnetic moments of paramagnetic salts where large distances suppress interactions between the moments. The large spatial separations are facilitated by water molecules, with a drawback of reduced stability of the material. Here, we show that the water-free frustrated magnet KBaYb(BO3)2 can be ideal for refrigeration, achieving at least 22 mK. Compared to conventional refrigerants, KBaYb(BO3)2 does not degrade even under high temperatures and ultra-high vacuum. Further, its magnetic frustration and structural randomness enable cooling to temperatures several times lower than the energy scale of magnetic interactions, which is the main limiting factor for the base temperature of conventional refrigerants.
suppression of thermal fluctuations by lowering temperature gives access to intricate and potentially usable quantum effects. Major discoveries, such as the quantum Hall effect and superfluidity and superconductivity, have been made by explorations of matter close to absolute zero. Recently, the development of quantum computers and sensors for dark matter detection rendered low-temperature refrigeration an important technological challenge. One of the viable methods for reaching zero external magnetic fields down to zero temperature, there are always weak but finite interactions in real materials. For many decades ever since Debye and Giauque independently proposed ADR, water-containing paramagnetic salts have been materials of choice for cooling in the mK range. In these materials, the interactions are reduced by large distances between the magnetic ions, which are separated by water molecules. However, an abundance of water makes these salts prone to structural disorder. The only advantage of \( ^3\text{He} – ^4\text{He} \) dilution refrigeration is its capability of continuous cooling while conventional ADR is a single-shot technique. This makes the \( ^3\text{He} – ^4\text{He} \) dilution refrigeration more commonly used than ADR. However, the situation may change thanks to recent developments of continuous ADR cooling and the availability of commercial continuous refrigerators based on ADR. Therefore, ADR has the potential of becoming the main cooling technology already in near future, at least in the mK temperature range.

ADR uses magnetic moments of almost-ideal paramagnets with very weak magnetic interaction \( J \). Because the interaction is weak, magnetic moments are easily aligned by the external magnetic field, causing a reduction of entropy (Fig. 1a, b). Even at zero external magnetic field \( H = 0 \), magnetic moments of such almost-ideal paramagnets experience some small internal magnetic field produced by adjacent magnetic moments through magnetic interactions. This causes a tiny Zeeman splitting and magnetic order at the same energy scale \( \Delta_0 \sim \Delta' \). Therefore, entropy, which is the driving force of ADR, decreases to zero below the temperature of \( T \sim \Delta' \), thus putting a limit on the end temperature \( T_e \) that can be reached via ADR with this material (Fig. 1b). As indicated by a black horizontal arrow in Fig. 1b, the entropy difference between \( H = 0 \) and \( H \neq 0 \) is the key for ADR. While a perfect paramagnet with zero magnetic interactions would be an ideal refrigerant, having maximum entropy at zero fields down to zero temperature, there are always weak but finite interactions in real materials.

For many decades ever since Debye and Giauque independently proposed ADR, water-containing paramagnetic salts have been materials of choice for cooling in the mK range. In these materials, the interactions are reduced by large distances between the magnetic ions, which are separated by water molecules. However, an abundance of water makes these salts prone to decomposition. They deliquesce in a humid atmosphere and dehydrate in vacuum or upon even mild heating. Therefore, for repeated use without degradation, stable water-free materials with very weak magnetic interactions are desirable. Furthermore, ADR would be certainly beneficial for applications in ultra-high-vacuum (UHV) apparatus, especially in scanning tunneling microscopy and angle-resolved photoemission spectroscopy where the necessity of chamber baking at high temperature and high vacuum for reaching UHV makes the use of current ADR materials essentially impossible. It is, therefore, desirable to find suitable ADR materials without water molecules.

One promising candidate for \( \text{H}_2\text{O} \)-free refrigerant is \( \text{KBaYb(BO}_3)_2 \) with magnetic \( \text{Yb}^{3+} \) ions. At sufficiently low temperatures, only the lowest Kramers doublet of \( \text{Yb}^{3+} \) is occupied in this material. In its crystal structure depicted in Fig. 1c, \( \text{YbO}_6 \) octahedra with \( \text{Yb}^{3+} \) magnetic moments are separated spatially within the \( \text{ab} \)-plane by \( \text{BO}_3 \) triangles. These negatively charged layers are interspersed along the \( \text{c} \)-axis by the positively charged \( \text{K}^+ \) and \( \text{Ba}^{2+} \) ions that occupy the single crystallographic site. The shorter \( \text{Yb}–\text{Yb} \) distances of 5.41 Å within the \( \text{ab} \) plane connect magnetic \( \text{Yb} \)-ions into a triangular lattice, the feature that already caused interest in this and isostructural rare-earth borates from the perspective of frustrated magnetism. The interplane \( \text{Yb}–\text{Yb} \) distances are only slightly longer (6.64 Å) and cause additional frustration because adjacent triangular layers are shifted relative to each other, as shown by solid lines in Fig. 1c. Such geometrical frustration may shift the magnetic ordering transition toward lower temperatures or even suppress the magnetic order completely. The distribution of \( \text{K}^+ \) and \( \text{Ba}^{2+} \) results in uneven electric fields acting on the magnetic \( \text{Yb}^{3+} \) ions and may lead to random exchange couplings that are also detrimental for the magnetic ordering. Sizable remaining entropy due to the suppression of the magnetic long-range order facilitates the cooling even below \( T \) (Fig. 1b). Moreover, the presence of soft modes in frustrated magnets amplifies the magnetocaloric effect and further lowers the end temperature of the cooling process.
Here, we demonstrate the effective refrigeration with the frustrated magnet KBaYb(BO₃)₂ that shows excellent ADR performance on par with conventional water-containing paramagnetic salts and achieves an end temperature Tₑ of at least 22 mK, starting from a temperature of 2 K at a magnetic field of 5 T. The H₂O-free refrigerant combines several properties that are beneficial for reaching lowest temperatures: the large separation between the magnetic ions, geometrical frustration of residual magnetic interactions, as well as their potential randomness.

Results
Magnetic properties. Magnetization measured down to 0.5 K shows the typical paramagnetic behavior (Fig. 2). Field-dependent magnetization is perfectly described by the Brillouin function augmented by the van Vleck function for J = ½ for the lowest Kramers doublet of Yb³⁺. The inset shows inverse magnetic susceptibility, 1/χ, measured at 0.1 T. Solid line is a linear fit in the 0.4 K ≤ T ≤ 2.0 K range, resulting in the effective magnetic moment µₑff = 2.28 µB and Curie-Weiss temperature θ = −60 ± 2 mK.

Fig. 2 Magnetic properties of KBaYb(BO₃)₂. The field-dependent magnetization of KBaYb(BO₃)₂ at 0.5 K. Solid line is a fit to the data with gBμBχ + xμB where g is the g-factor, J = ½ for the lowest Kramers doublet of Yb³⁺, and B is the Brillouin function for J = ½ with x = (gμBμBχ) = (KB). The second term is due to the van Vleck susceptibility χ. The fit returns g = 2.54 and x/μB/μB = 0.0111 µB⁻¹. The inset shows inverse magnetic susceptibility, 1/(χ − χ₀) corresponding to the Curie–Weiss law. The fit returns the effective magnetic moment µₑff = 2.28 µB and Curie–Weiss temperature θ = −60 ± 2 mK. We note that the reduced effective magnetic moment from free Yb³⁺ is due to crystalline electric field effect. We show in Supplementary Fig. 1 that at high temperatures µₑff recovers the free-ion value for Yb³⁺. The small value of θ indicates that temperatures on the order of 10 mK would be needed to explore cooperative magnetism and frustrated magnetic behavior of KBaYb(BO₃)₂, making this material a quite challenging system to study in comparison with YbMgGaO₄ and Yb³⁺ delafossites having Curie–Weiss temperatures of several Kelvin. On the other hand, KBaYb(BO₃)₂ itself can be used to reach these extremely low temperatures, as we show below.

Specific heat. First hints for the ADR potential of KBaYb(BO₃)₂ are found in the magnetic specific heat data Cₓm(T) that were obtained via subtracting the lattice contribution given by the nonmagnetic reference compound KBaLu(BO₃)₂ (Fig. 3a). In zero field, specific heat increases toward lower temperatures, as we show below.

Refrigeration test under the near-adiabatic condition. We test this prediction in the actual cooling experiment that was performed with a 4.02 g pellet containing equal weights of KBaYb(BO₃)₂ and silver powder (10–50 μm particle size). Silver improves thermal conductivity within the pellet of insulating KBaYb(BO₃)₂. To improve thermal conduction between the particles, we sintered the pressed pellet at 600 °C. The pellet was mounted on a sapphire-plate sample holder, which is held on a plastic frame by four 50 μm thin fishing wires. A resistive RuO₂ thermometer is attached to the pellet with glue. To suppress the thermal conduction from the heat bath, thin superconducting filaments are used as wire leads on the resistive thermometer for temperature measurements. This setup was attached to the cold
bath in a vacuum chamber (with the pressure of \( \sim 10^{-6} \) mbar) of the \(^3\)He–\(^4\)He dilution refrigerator.

In order to minimize the heat flow into the sample from the bath, we used a feedback control of the bath temperature \( T_b \) to follow the sample temperature \( T_s \). Because the heat flow is \( Q = \kappa \Delta T \) where \( 
abla = T_b - T_s \) and \( \kappa \) is the thermal conductance between the bath and the pellet, minimizing \( \Delta T \) suppresses \( Q \) significantly. With the bath temperature of 2 K, the pellet was slowly cooled to 2 K at \( \mu_0 H = 5 \) T. Then we swept the magnetic field to zero with the 0.25 T min\(^{-1} \) rate while giving the feedback control to the bath. As shown in Fig. 4, the pellet is quickly cooled down to less than 22 mK, which is the lowest limit of the thermometer calibration. By extrapolating this calibration to lower temperatures (see Supplementary Fig. 3), we find the end temperature of about 16 mK. A small spike appearing around \( T = 80 \) mK (\( \mu_0 H = 0.1 \) T) is probably due to the magnetic flux pinning of the superconducting magnet. After reaching the lowest temperature, the sample warms up slowly due to the heat flow from the surroundings (the bath and radiation). Note that \( T_b \) deviates from \( T_s \) below 0.4 K. This is because the cooling rate of \( T_s \) is too fast for the bath to follow. The large temperature difference indicates a weak thermal conductance between the sample and the bath. Because of the difference, there is finite heat flow into the sample. Therefore, under ideal adiabatic conditions, the end temperature would be even lower than the extrapolated 16 mK.

We note that there is no visible anomaly in sample temperatures other than the spike at 80 K. A phase transition of second (or first) order would cause a kink (or a local plateau). The absence of such an anomaly confirms the absence of magnetic ordering in KBaYb(BO3)_2 at least down to 22 mK and most likely down to about 16 mK, the temperature several times lower than \( |\theta| = 60 \) mK. This behavior is in line with the geometrical frustration expected in KBaYb(BO3)_2. Assuming \( \theta = -\frac{1}{2} J \) in a nearest-neighbor triangular antiferromagnet and \( T_N/J \approx 0.2 \) reported for Co-based frustrated materials\(^{25} \), we estimate \( J \approx 40 \) mK and \( T_N \approx 8 \) mK, which would be comparable with the end temperature of 16 mK achieved in our cooling experiment.

**Discussion**

We conclude that KBaYb(BO3)_2 can be highly efficient in ADR while containing no water molecules and showing excellent stability upon both exposures to air and heating. Key parameters of the ADR materials are compared in Table 1. Figure 3
illustrates that even with the moderate field of 5 T almost all entropy \( R \ln 2 \) of the lowest Kramers doublet is used for the ground state as \( S_{GS} \). From the absolute values of \( S_{GS} \) divided by volume, KBaYb(BO3)\(_2\) is clearly competitive with MAS and FAA as “high-temperature” paramagnetic salts that develop magnetic order below \( T_m \) of 170 and 30 mK, respectively, and thus cannot cool below these temperatures. The lower-temperature ADR comes at the cost of the higher dilution of the magnetic ions and, therefore, lower \( S_{GS}/\text{Vol.} \) in CPA and especially CMN. It is in fact natural that the high density of the magnetic moments and low magnetic ordering temperature are unlikely to coexist. Nevertheless, KBaYb(BO3)\(_2\) combines these mutually exclusive properties by virtue of its magnetic frustration and structural randomness that both help to suppress \( T_m \) well below the energy scale of magnetic interactions given by \( |\theta| = 60 \text{ mK} \). The material also shows an outstanding density of magnetic ions, 6.7 nm\(^{-3}\), which is much higher than in any of the paramagnetic salts and would allow the design of more compact ADR apparatus. Even higher density has been reported for YbPt2Sn and YbGa2O12 that, however, develop magnetic order below 0.25 K and long-range order below 2 K.

### Methods

#### Sample preparation and characterization

Powder samples of KBaYb(BO3)\(_2\) were prepared by a solid-state reaction of K\(_2\)CO\(_3\), BaCO\(_3\), Yb\(_2\)O\(_3\), and H\(_3\)BO\(_3\) taken in stoichiometric amounts, with the 6% excess of H\(_2\)BO\(_3\) and 2% excess of K\(_2\)CO\(_3\) and BaCO\(_3\). The reactants were carefully ground, placed into alumina crucibles, and kept at 200 °C for 6 h to remove absorbed water. They were subsequently annealed at 700 °C for 24 h, re-ground, and re-annealed at 900 °C for another 24 h. All annealing steps were performed in the air. Sintered powders of KBaYb(BO3)\(_2\) were ground and pressed into small pellets with the mass of 18.4 and 2.69 mg used for measurements of magnetic susceptibility and specific heat, respectively.

X-ray powder diffraction pattern was recorded at room temperature using the Empyream diffractometer from PANalytical (CuK\(_\alpha\), radiation, reflection mode). Rietveld refinement (Supplementary Fig. 4) confirmed the formation of KBaYb(BO3)\(_2\) with the lattice parameters \( a = 5.4112(2) \) Å and \( c = 17.5926(2) \) Å and atomic positions shown in Supplementary Table 1, in good agreement with the earlier report\(^{26}\). Several very weak peaks of Yb\(_2\)O\(_3\) were detected, corresponding to 0.75(1) wt% of the impurity phase.

Considering that only 0.75(1) wt% of the Yb\(_2\)O\(_3\) impurity is contained in the sample, and the magnetic ordering transition of Yb\(_2\)O\(_3\) is at 2.3 K\(^{23}\), we infer that the anomaly should have a different origin. On the other hand, the small amount of entropy suggests that it is unrelated to KBaYb(BO3)\(_2\) itself. The most plausible explanation would be the presence of an amorphous or weakly crystalline impurity that is not seen in X-ray diffraction. Note also that a similar anomaly has been reported for the isostructural compound NaYb(BO3)\(_2\)\(^{25}\).

#### Measurements and tests at low temperatures

Magnetic susceptibility was measured by an MPMS SQUID magnetometer from Quantum Design equipped with a \(^3\)He-refrigerator. Measurements of specific heat in the temperature range from 12 K down to 400 mK were performed by using a Quantum Design, PPMS, equipped with a \(^3\)He-refrigerator insert. Specific heat measurements of quasi-adiabatic heat pulse method at the lowest temperature down to 50 mK and the tests for ADR with this material have been performed, using a \(^3\)He–\(^4\)He dilution refrigerator and PPMS.

Extrapolation of thermometer calibration. A ruthenium oxide thermometer is used for the tests of ADR with KBaYb(BO3)\(_2\). It is calibrated down to 22 mK. For temperatures below this lower limit, we have used an extrapolation of the calibration to lower temperatures. Supplementary Fig. 3 shows the extrapolation. Since \( T_m \) is related to \( \ln (R – R_0) \) where \( R_0 \) is the resistance at room temperature, it is expected that the temperature increases with increasing temperature.

### Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

Y.T., A.A.T. and P.G. conceived and designed the study. Y.T. and S.B. performed the specific heat measurements, the tests using dilution refrigerator and PPMS. K.K. and A.J. performed the magnetic susceptibility measurements. K.K. and A.J. prepared and characterized the samples. Y.T., S.B., A.A.T., and P.G. discussed the results. Y.T. and A.A.T. prepared the paper.

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Competing interests

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Additional information

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Correspondence and requests for materials should be addressed to Y.T.

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