Precision determination of the ground-state hyperfine splitting in a $^{113}Cd^+$ microwave clock

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Abstract*—As a candidate for the next generation microwave clock, microwave atomic clocks based on trapped ions are currently studied worldwide. Since 2010, our team at Tsinghua University has been committed to developing a high-performance $^{113}Cd^+$ microwave ion clock. In 2021, the laser-cooled cadmium-ion microwave clock constructed in our laboratory demonstrated remarkable performance, with a short-term instability of $4.2 \times 10^{-13}/\sqrt{\tau}$ and a relative frequency uncertainty of 1.8×10^{-14}, improving nearly three orders of magnitude compared to the result from JPL. The ground-state hyperfine splitting of $^{113}Cd^+$ was determined to be 15199862855.02799(27) Hz, currently the most accurate measurement result for this transition frequency. Apart from that, we introduced the sympathetic cooling technology into the experiment of cadmium-ion microwave clock. Using $^{40}Ca^+$ as the coolant ion, we obtained Ramsey patterns with a free evolution time of up to 100 seconds, ultimately improving the short-term instability of the system to $3.48 \times 10^{-13}/\sqrt{\tau}$.

Keywords—cadmium-ion microwave clock, linear Paul trap, laser cooling, sympathetic cooling

I. Introduction

The atomic clock is an instrument that achieves precise frequency output based on the transition frequency of atoms or ions. The transition frequency between two energy levels of an atom is an inherent property that remains constant in the absence of external disturbances. Depending on the operating frequency, atomic clocks can be divided into two main categories: microwave atomic clocks and optical atomic clocks. Among them, optical atomic clocks surpass microwave atomic clocks in terms of accuracy and stability. However, due to factors such as size and cost, optical atomic clocks are currently mainly applied in fundamental research [1-2]. Microwave atomic clocks have a relatively simple structure, and low-cost, compact-volume microwave atomic clocks can be tailored to different needs. They remain the primary frequency standard used in timekeeping, synchronization, and navigation. Compared to neutral atoms, microwave atomic clocks based on trapped ions have advantages in miniaturization and stability, making them widely researched and considered candidates for the next generation of commercial practical microwave clocks. Commonly used ions in the development of microwave ion clocks include $^{199}Hg^+$, $^{171}Yb^+$ and $^{113}Cd^+$, with corresponding clock transition frequencies of 40.5 GHz, 12.6 GHz and 15.2 GHz, respectively. Larger clock transition frequencies correspond to higher expected performance.

Compared to $^{199}Hg^+$ and $^{171}Yb^+$, there has been relatively less investigation into $^{113}Cd^+$. The nuclear spin of $^{113}Cd^+$ is 1/2, and its upper level $^2P_{3/2}$ hyperfine splitting is 800 MHz. Only a 214.5 nm laser is needed to cool, pump, and detect the ion, demonstrating the potential for miniaturization. In 1996, Tanaka et al. from Japan employed a buffer-gas cooling scheme and measured the ground-state hyperfine splitting frequency of $^{113}Cd^+$ as 15199862858(2) Hz with a relative frequency uncertainty of 1.3×10^{-10} [3]. In 2006, Jelenković et al. improved the measurement uncertainty to 1.3×10^{-11} via a microwave optical double resonance technique, where the ions were also cooled by buffer gas, and pumped and detected by a discharge lamp. They also estimated the instability of their $^{113}Cd^+$ clock to be $2 \times 10^{-13}/\sqrt{\tau}$, but no experimental data were reported [4].

Since 2010, our team at Tsinghua University has been committed to developing a high-performance cadmium-ion microwave clock. In 2015, we implemented closed-loop locking of the cadmium-ion microwave clock system, achieving a short-term instability of $6.1 \times 10^{-13}/\sqrt{\tau}$ [5]. Apart from that, we measured the ground-state hyperfine splitting frequency of $^{113}Cd^+$ to be 15199862855.0192(10) Hz, with a relative frequency uncertainty of 6.6×10^{-14} [5]. Subsequently, we further optimized the system and introduced the sympathetic cooling technique into the study of the cadmium-ion microwave clock. This paper reports the latest progress made by our team at Tsinghua University in the research on cadmium-ion microwave clocks.

II. Experimental Setup and Results

A. Laser-cooled cadmium-ion microwave clock

The relevant energy level structure of $^{113}Cd^+$ is shown in Fig. 1. The ions are cooled and detected by a 214.5-nm red detuned laser via the cycling transition between the states of $|^2S_{1/2}, F=1, m_F=1\rangle$ and $|^2P_{3/2}, F=2, m_F=2\rangle$. During laser cooling, ions may transition to the energy level of $|^2P_{3/2}, F=1\rangle$ because of the relatively small frequency difference between the states of $|^2P_{3/2}, F=1\rangle$ and $|^2P_{3/2}, F=2\rangle$. Part of the ions will fall to the energy of $|^2S_{1/2}, F=0\rangle$ through radiation. Therefore, a cooling laser with circular polarization connecting two Zeeman sublevels of the cycling transition is applied. In addition, microwave radiation of 15.2 GHz is applied to repump the ions from the dark state of $|^2S_{1/2}, F = 0\rangle$. Because the hyperfine splitting frequency of $|^2P_{3/2}\rangle$ is only 800 MHz, the pump laser beam is

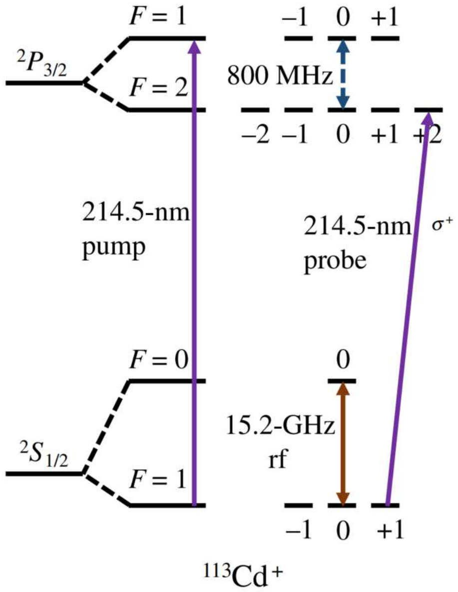

Fig. 1. Relevant energy-level structure of $^{113}Cd^+$.

generated by blue-shifting the cooling laser beam using acousto-optic modulators (AOMs). The frequency difference between the states of $|^2S_{1/2}, F = 0, m_F = 0\rangle$ and $|^2S_{1/2}, F = 1, m_F = 0\rangle$ is the chosen transition frequency, which is approximately 15.2 GHz.

In 2020, we designed and constructed a new cadmium-ion microwave clock system (Fig. 2). The core of the entire system is a linear quadrupole ion trap. Details of the ion trap are given in [6]. Each electrode is divided into three segments: the middle segment acts as radio frequency (RF) electrodes for radial confinement of ions, and the two ends act as end-cap (EC) electrodes for axial confinement. The radius of each electrode is 7.1 mm. The minimum distance from the nodal line of the trap to the electrode surface is 6.2 mm. The ion trap is horizontally mounted in a stainless-steel vacuum chamber. The pressure in the vacuum chamber is maintained below 1.5×10^{-11} mbar by an ion pump. A high-performance magnetic shield barrel composed of five layers of permalloy and a layer of soft iron around the vacuum chamber is used to minimize stray magnetic fields. In addition, the barrel is motor driven to move up and down. After active shielding, the magnetic field fluctuation in the center of the trap is reduced to less than 0.1 nT. Three pairs of Helmholtz coils were fixed around the vacuum chamber to generate a static magnetic field to split the Zeeman sublevels and to compensate for any residual magnetic field.

The Ramsey's method of separated oscillatory fields was employed to acquire the clock transition spectrum. The typical Ramsey fringe is shown in Fig. 3. The cooling time was set to 500-ms, with two microwave pulses each lasting 60-ms and spaced 500-ms apart, followed by a fluorescence detection time of 400-ms. In the experiment, the signal-to-noise ratio (SNR) of the clock transition spectrum was approximately 40. During the closed-loop locking process, the frequency synthesizer (E8257D) was referenced to the local oscillator (LO). The fluorescence intensity at the half-maximum points on both sides of the central peak of the Ramsey pattern for $^{113}Cd^+$ was measured, and the frequency deviation between the LO and the ion was calculated. This deviation was fed back to the LO through proportional-integral (PI) control, resulting in

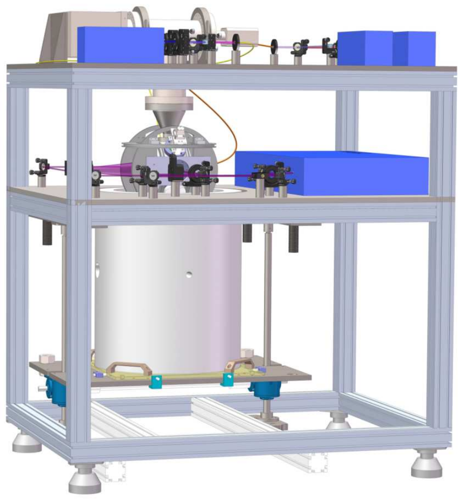

Fig. 2. Schematic diagram of the cadmium-ion microwave clock system.

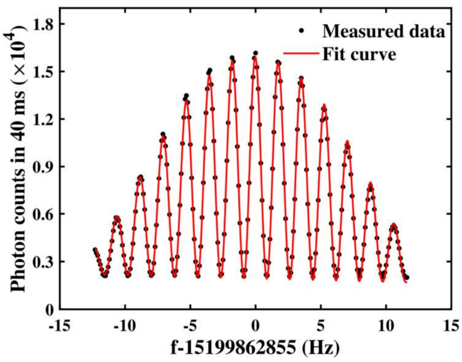

Fig. 3. Typical Ramsey fringe pattern obtained with a 500-ms cooling time, a 50-ms pump time, two phase-coherent microwave pulses of 60-ms duration separated by a free evolution time of 500-ms, and a fluorescence signal integration time of 400-ms. The cycle time to collect a point is 1.59 s. The scanning step is 0.1 Hz. The solid line is a nonlinear fit obtained from the experimental data.

the locking of the local oscillator's output frequency to the ion spectrum. Finally, the output frequency of the LO was compared with that of a hydrogen clock to obtain the frequency stability of the cadmium-ion microwave clock, as shown in Fig. 4.

The loop time is 3.18 s, which is the time to collect the error data at the half height of the central peak of the Ramsey fringe pattern, and corresponds to the time constant. Allan deviations longer than the time constant stem from the cadmium ions of the clock; those shorter than the time constant stem from the LO itself. After a long duration making comparisons, the fractional frequency stability of the $^{113}Cd^+$ microwave ion clock was estimated to be $4.2 \times 10^{-13}/\sqrt{\tau}$ [7], which reduces by nearly half that of the previous one [5]. Under the current experimental parameters with a loop time of 3.18 s, the fractional frequency stability limit due to the Dick effect is $3.43 \times 10^{-13}/\sqrt{\tau}$ [8], which implies that the noise of the LO is already the main factor limiting the short-term stability of the $^{113}Cd^+$ microwave ion clock.

The main systematic frequency shifts and their uncertainties of the $^{113}Cd^+$ microwave ion clock are listed in TABLE I. Among them, the second-order Zeeman frequency shift and the second-order Doppler frequency shift are two primary factors limiting the uncertainty of the system. The

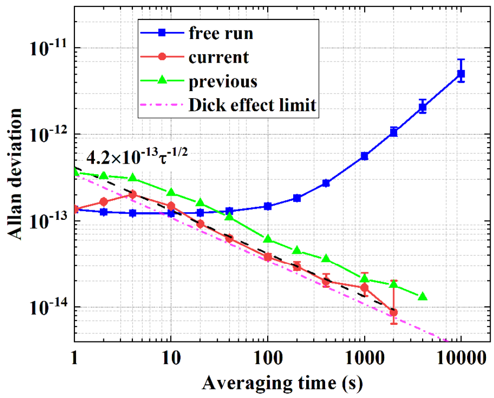

Fig. 4. Allan deviations of the $^{113}Cd^+$ microwave ion clock. The solid blue line is a fitting of data from the free-running local oscillator, the solid red line is that after closed-loop locking, and the pink dotted line signifies the Dick effect limit. The short-term fractional frequency stability of the clock is estimated to be $4.2 \times 10^{-13}/\sqrt{\tau}$.

uncertainty of the second-order Zeeman frequency shift is primarily attributed to fluctuations in the geomagnetic field, which can be minimized by enhancing the performance of the magnetic shielding device. The uncertainty of the second-order Doppler frequency shift arises mainly from the secular motion of trapped ions. The continuous reduction in the number of ions and the heating of ions during the microwave interrogation process also play a role. By employing multipole ion traps to position ions as closely as possible along the axis of the ion trap, the excess micromotion of trapped ions can be reduced. Another approach is to use ions with a mass number greater than that of $^{113}Cd^+$ for sympathetic cooling of $^{113}Cd^+$, ensuring sustained cooling of $^{113}Cd^+$ ions during the microwave interrogation process.

In our experiment, the frequency measurement is referenced against an active hydrogen clock, and that the fractional frequency difference between this active hydrogen clock and coordinated universal time (UTC) was measured by the method of GPS common-view, the difference between UTC and the primary frequency standards (PFSs) was also considered. To obtain the ground-state hyperfine transition frequency of $^{113}Cd^+$, the majority of the systematic frequency shifts and corresponding frequency uncertainties have been evaluated carefully. Ultimately, the ground-state hyperfine splitting frequency of $^{113}Cd^+$ was determined to be 15199862855.02799(27) Hz, with a relative frequency shift uncertainty of 1.8×10^{-14} [7]. TABLE II lists all the measurement results of the ground-state hyperfine splitting frequency for $^{113}Cd^+$. Our measurement result was consistent with previous results. To the best of our knowledge, the measurement accuracy is currently the highest among all laser-cooled $^{113}Cd^+$ microwave atomic clocks.

B. Sympathetically-cooled cadmium-ion microwave clock

The performance improvement of laser-cooled cadmium-ion microwave clocks is subject to certain limitations: firstly, during the microwave interrogation, effective cooling of cadmium ions cannot be achieved, resulting in an increase in ion temperature; secondly, the cooling process belongs to the system's dead time, which is unavoidable. Thus, we introduced the technology of sympathetic cooling into the cadmium-ion microwave clock. The basic principle of sympathetic cooling relies on the Coulomb interaction between ions, realizing continuous cooling of one type of ion

TABLE I. Estimated systematic frequency shifts and uncertainties of laser-cooled $^{113}Cd^+$ microwave ion clock.

Shift	Magnitude (10^{-15})	Uncertainty (10^{-15})
Second-order Zeeman shift	105720	3
Second-order Doppler shift	-65.9	3.6
BBR Stark shift	-0.1815	<0.1
BBR Zeeman shift	-0.00981	<0.01
Gravitational red shift	4.7	0.1
Pressure shift	0	<0.1
Light shift	0	0
Total	105658.6	4.6

TABLE II. Comparison of different measurement results of $^{113}Cd^+$ hyperfine splitting of the ground state.

Group	Measurement result (Hz)	Uncertainty
Japan (1996)	15199862858(2)	1.3×10^{-10}
JPL (2006)	15199862855.0(2)	1.3×10^{-11}
THU (2012)	15199862854.96(12)	7.9×10^{-12}
THU (2013)	15199862855.0125(87)	5.7×10^{-13}
THU (2015)	15199862855.0287(10)	6.6×10^{-14}
THU (2021)	15199862855.02799(27)	1.8×10^{-14}

(target ion, sympathetic cooling) by another type of ion (coolant ion, laser cooling). Compared to laser-cooled microwave ion clocks, sympathetically-cooled microwave ion clocks have the following advantages: first, there is no need for the laser cooling process, reducing the dead time of the loop and effectively lowering the Dick effect; second, continuous cooling extends the coherence time of ions, further narrowing the linewidth of clock transition; third, maintaining the low-temperature state of target ions continuously reduces the Doppler frequency shift and its uncertainty of ions.

In 2018, we used $^{24}Mg^+$ as the coolant ion, achieving sympathetic cooling of a large mixed ion crystal containing approximately 3.3×10^5 ions [9]. However, $^{24}Mg^+$ ions easily react with hydrogen gas in the background, generating MgH^+ dark ions, which cannot be used for long-term cooling of $^{113}Cd^+$ ions. In 2019, we changed the coolant to the more stable $^{40}Ca^+$ ion [10]. Fig. 5 shows the experimentally obtained $^{40}Ca^+$ - $^{113}Cd^+$ two-component ion crystal [11]. Fig. 5(a) is an image without a filter; Fig. 5(b) is a picture taken separately under filters corresponding to the two ions, later synthesized and subjected to simple color correction; Fig. 5(c) is the result obtained from molecular dynamics (MD) simulation, consistent with the experiment results [12]. In the two-component ion crystal, the lighter $^{40}Ca^+$ forms an ellipsoidal structure at the center, while the heavier $^{113}Cd^+$ surrounds the $^{40}Ca^+$ ellipsoid, forming a hollow cylindrical structure. Under sympathetic cooling conditions, a typical temperature of 80 mK was measured for the $^{113}Cd^+$ ion cloud through 214.5 nm detection light scanning. In addition, optimization was performed on the RF voltage and EC voltage during the experiment.

Using sympathetic cooling technology, we obtained Ramsey fringes with a maximum free evolution time of up to

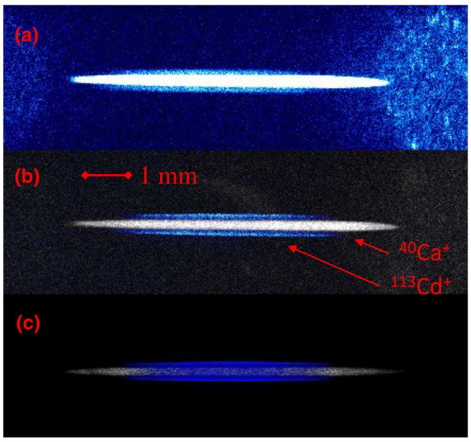

Fig. 5. Typical image of $^{40}Ca^+$ - $^{113}Cd^+$ two-component ion crystal. In these images, $^{40}Ca^+$ ions appear white and $^{113}Cd^+$ ions appear blue. (a) Image taken by EMCCD without UV filters. (b) Image synthesized from ion images under different wavelength filters, taking into account the chromatic aberration effects. (c) Simulation image of the two-component ion crystal under the same conditions as for (a) and (b).

100 seconds. Considering that the SNR of the signal decreases as the free evolution time increases, a free evolution time of 5 seconds was set during closed-loop locking in the experiment. The loop time was approximately 11 seconds, and the short-term frequency stability of the $^{40}Ca^+$ - $^{113}Cd^+$ cadmium-ion microwave clock was measured to be $3.48 \times 10^{-13}/\sqrt{\tau}$ [11]. Compared to the optimal short-term frequency stability of a laser-cooled cadmium-ion microwave clock [7], the sympathetically-cooled cadmium-ion microwave clock demonstrates nearly twice the performance in short-term frequency stability. In comparison to NIST's laser-cooled $^{199}Hg^+$ microwave clock [13], the short-term frequency stability of the sympathetically-cooled $^{113}Cd^+$ microwave clock is similar, despite the clock transition frequency of $^{113}Cd^+$ being only one-third that of $^{199}Hg^+$.

III. Conclusion

As a candidate for the next generation practical microwave clock, microwave atomic clocks based on trapped ions are currently a research focus in the field of atomic clocks worldwide. The $^{113}Cd^+$ ion has attracted extensive attention due to its advantages, such as requiring fewer laser beams and having a large hyperfine splitting frequency. Since 2010, our team at Tsinghua University has been consistently devoted to building a high-performance cadmium-ion microwave clock. Using laser cooling technology, the cadmium-ion microwave clock constructed in our laboratory demonstrated outstanding performance, with a short-term instability of $4.2 \times 10^{-13}/\sqrt{\tau}$ and a relative frequency uncertainty of 1.8×10^{-14}, improving nearly three orders of magnitude compared to the result from JPL. Additionally, the 0-0 ground-state hyperfine splitting frequency of $^{113}Cd^+$ was determined to be 15199862855.02799(27) Hz, currently the most accurate measurement result in the world. To further improve the short-term stability of the cadmium-ion microwave clock, we introduced the sympathetic cooling technology into the experiment. Using $^{40}Ca^+$ as the coolant ion, we obtained Ramsey patterns with a free evolution time of up to 100 seconds, ultimately improving the short-term stability of the cadmium-ion microwave clock to $3.48 \times 10^{-13}/\sqrt{\tau}$, showcasing the advantages of microwave ion clocks based on sympathetic cooling scheme.

Overall, the results obtained by our team at Tsinghua University enrich the studies of microwave ion clocks and advancing the transition of microwave ion clocks towards commercial practical microwave clocks.

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