

CrK(SO₄)₂·12H₂O 晶体的生长及其磁制冷性能

陈语葳^{1,2}, 刘 萍¹, 刘 旺^{1,2}, 王 昌¹, 戴 巍¹, 沈 俊¹, 张国春^{1,2}, 涂 衡^{1,2}

(1. 中国科学院理化技术研究所, 北京 100190; 2. 中国科学院大学材料科学与光电工程中心, 北京 100049)

摘 要: 顺磁盐在超低温制冷方面具有绝对优势, 且在极低温度下使用时往往是其水合盐类晶体, 对水合盐类磁制冷材料的探索意义重大。本工作采用缓慢降温法生长出尺寸为 32 mm×32 mm×20 mm 的 CrK(SO₄)₂·12H₂O (CPA) 单晶, 分析了生长条件与晶体形貌之间的相互关系, 研究了 CPA 的热稳定性和磁热性能。结果表明, CPA 在温度为 2 K、外加磁场强度为 7 T 条件下, 表现出大的磁热效应, 磁熵变值达到 29.75 J·kg⁻¹·K⁻¹。在密集排布铜线的密封容器中生长 CPA 晶体, 并将其用于 2 级单冲程绝热去磁制冷系统中, 空载条件下制冷温度达到 90 mK。

关键词: 晶体生长; 晶体形貌; 顺磁盐材料; 磁热效应

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Growth and Characterization of CrK(SO₄)₂·12H₂O Crystals Used in Magnetic Adiabatic Refrigerator

CHEN Yuwei^{1,2}, LIU Ping¹, LIU Wang^{1,2}, WANG Chang¹, DAI Wei¹, SHEN Jun¹, ZHANG Guochun^{1,2}, TU Heng^{1,2}

(1. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China; 2. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: Paramagnetic salts perform satisfactorily in cryogenic refrigeration, and hydrated salt crystals are usually used as refrigerated materials at a rather low temperature. In this paper, a chromium potassium alum CrK(SO₄)₂·12H₂O (CPA) single crystal with the size of 32 mm×32 mm×20 mm was grown by a slow cooling method. The relationship between the growth condition and crystal morphology was analyzed, and the thermal behavior, infrared spectrum, and magnetic performance of CPA crystal were also investigated. The results reveal that the CPA crystal exhibits a magnetocaloric effect up to 29.75 J·kg⁻¹·K⁻¹ in an applied magnetic field of 7 T at 2 K. A salt pill made by growing the CPA crystals on an array of copper wires in a sealed container was used in a two-stage single-shot adiabatic demagnetization refrigerator, obtaining a no-load temperature of 90 mK.

Keywords: crystal growth; crystal morphology; paramagnetic materials; magnetocaloric effect

1 Introduction

Magnetic refrigeration technology based on the magnetocaloric materials has important application prospects due to the great efficient, low energy consuming, and environment friendly^[1]. In particular, the adiabatic demagnetization refrigerator (ADR) using paramagnetic salts as a working medium is one of the ideal methods to generate the sub-Kelvin temperatures^[2]. Compared with other technologies like

dilution refrigeration and absorption refrigeration, ADR has the maximum thermodynamic efficiency and can work under zero-g environment as a promising technology for compact sub-Kelvin applications both in space and on the ground^[3].

Among the paramagnetic salts, hydrated salts containing iron group elements, such as CrK(SO₄)₂·12H₂O (CPA), FeNH₄(SO₄)₂·12H₂O (FAA), and Mn(NH₄)₂(SO₄)₂·6H₂O (MAS)^[4], are usually used as the working materials in an extremely low temperature down to the milli-Kelvin limit due to their

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第一作者: 陈语葳(1997—), 女, 博士研究生。

通信作者: 涂 衡(1982—), 男, 博士, 副研究员。

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First author: CHEN Yuwei (1997—), female, Doctorial candidate.

E-mail: chenyuwei19@mails.ucas.ac.cn

Correspondent author: TU Heng (1982—), male, Ph.D., Associate Professor.

E-mail: tuheng@mail.ipc.ac.cn

relatively low ordering temperature^[5-6]. According to Lipson and Beevers^[7], CPA adopts the α -alum structure with cubic $Pa\bar{3}$ space group (No. 206). CPA is a classic paramagnetic salt used as a refrigerant of adiabatic demagnetization refrigerator (ADR) because of its low Curie point (*i.e.*, 9 mK)^[8] since magnetic Cr^{3+} ion has a d^3 electronic configuration and its ground state spin quantum number J is 3/2. In 2015, a fast thermal response miniature CPA salt pill for use in a milli-Kelvin cryocooler was designed, demonstrating its promising potential for continuous cooling^[9].

There are a few systematic reports on the growth of the large size CPA single crystal so far^[10-11]. Also, the growth technique of CPA crystals applied to ADR has not been independently mastered. This paper was thus to investigate the growth, morphology, and properties of the CPA crystal. Moreover, a CPA pill was used in a two-stage single-shot ADR for a no-load temperature of 90 mK.

2 Experimental

2.1 Single crystal growth

A reagent CPA with analytical grade was gained from Aladdin Reagent Co., China. The solubility of CPA in water is an important parameter for the crystal growth. Fig. 1 shows the corresponding measured solubility at different temperatures, and the measured values are consistent with those reported in the literatures^[9, 12]. In Fig. 1, an appropriate concentration of CPA aqueous solution is 23.31 g/(100 mL) when the crystals are grown *via* evaporation at room temperature (*i.e.*, 20 °C). The CPA crystals can be also grown by a cooling method at 44–35 °C with a higher concentration of CPA solution in water (*i.e.*, 92.39–56.43 g/100 mL), which is beneficial for obtaining the large crystals.

In order to prepare the seed crystals, a saturated solution (*i.e.*, 46.62 g CPA, 200 mL H_2O) was put in

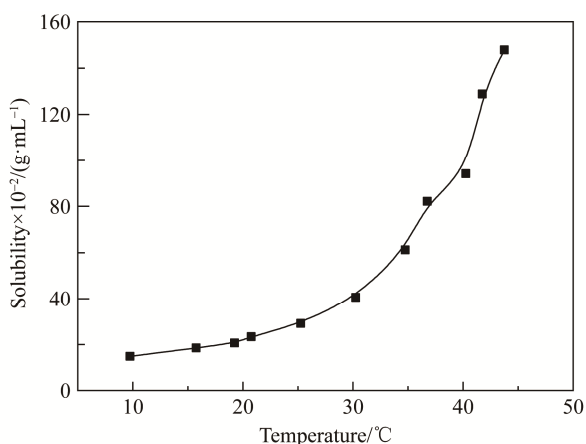


Fig. 1 Solubility of CPA in deionized water at different temperatures

air at room temperature (*i.e.*, 20 °C). When the solvent was evaporated naturally, the crystals with different shapes and volumes (see Fig. 2) were obtained *via* spontaneous nucleation, which were used as the seeds to grow bulky crystals. The bulky single crystals were grown by the seed crystal method to avoid the restrictions from other crystals and walls of a beaker. A small single crystal with a clear shape was chosen as a seed. The seed was fixed on one end of a platinum wire. The glass rod connected with the platinum wire was put on a glass beaker to keep the position of the seed stable. In the process of slow evaporation at room temperature (*i.e.*, 20 °C), a near octahedron crystal with the side lengths of 16 mm (see Fig. 2(c)) was obtained from a saturated solution in water (23.31 g CPA, 100 mL). The platinum wire immersed in the solution was completely wrapped by the crystals.

The larger crystals were grown by a slow cooling method. Fig. 3 shows the schematic diagram of the crystal growth device. The saturated solution in water (985.41 g CPA, 1 200 mL) at 36.5 °C was put into a sealed container under stirring, and then placed the container in a water bath. A seed crystal was immersed in solution at the saturation temperature, which was determined by a trial seed crystal method. The rotation rate and cooling rate were 30 r/min and 0.1 °C/d, respectively. After 40 d, a complete black-purple single crystal with the size of 32 mm×32 mm×20 mm (see Fig. 2(d)) was obtained.

Moreover, in a special container with an array of copper wires, CPA crystals of 21.33 g were crystallized from the saturated solution at 36.5 °C and the same cooling rate. The filling fraction of CPA crystals was 92%, which was used in an experimental two-stage ADR.

2.2 Characterizations

Powder X-ray diffraction (XRD) pattern of CPA crystal was measured on a model Bruker D8 X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) at room temperature (*i.e.*, 25 °C) in the 2θ range of 10°–60°. The scanning step width and scanning rate are 0.01° and 0.05(°)/s, respectively. The infrared spectrum (IR) of the samples was recorded on a model Excalibur 3100 infrared spectrophotometer in the 400–4 000 cm^{-1} wavenumber range. The sample and dried KBr as a reference were thoroughly mixed in a weight ratio of 1:100.

The thermal stability of CPA crystal was analyzed by a model LabsysTM TG-DTA16 thermal analyzer. The sample was heated from room temperature to 500 °C at a rate of 10 °C/min.

The temperature- dependent magnetization at 2–200 K was measured by a model Quantum Design PPMS-9 magnetic analyzer at a magnetic field of 3 T. The lowest measurable temperature of PPMS is 2 K. The mass of CPA single crystal sample is 14.94 mg.

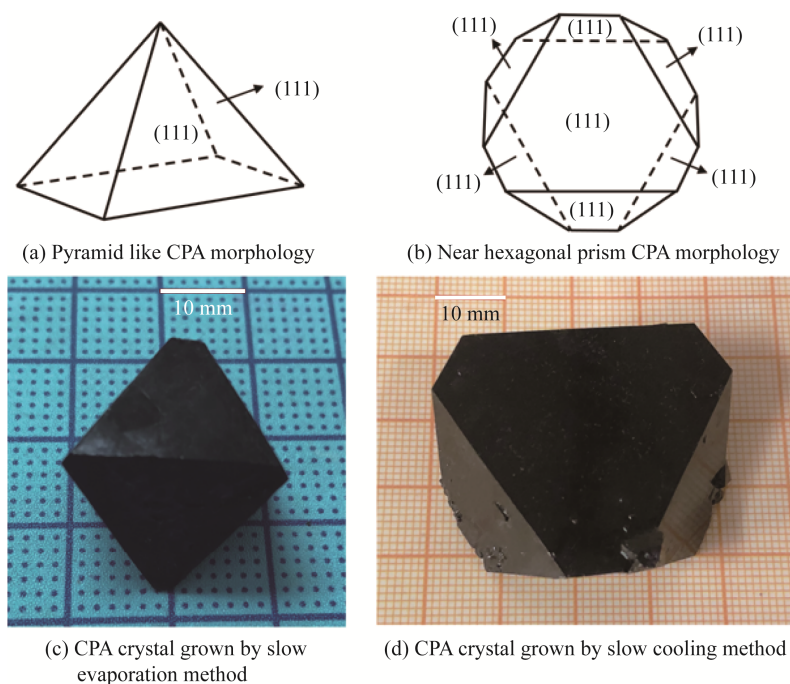


Fig. 2 Two morphologies of CPA and single crystals obtained by different methods

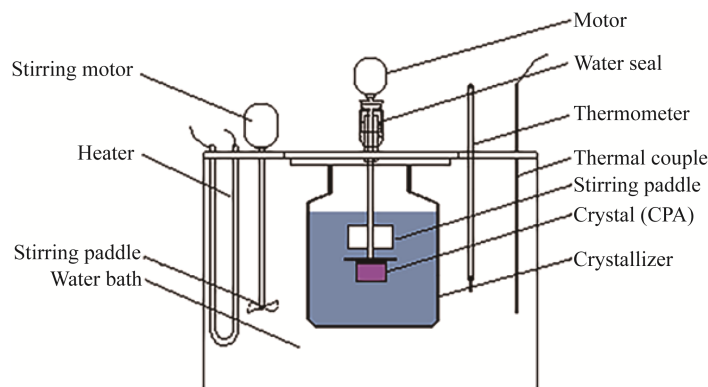


Fig. 3 Schematic diagram of device for the seed crystal method

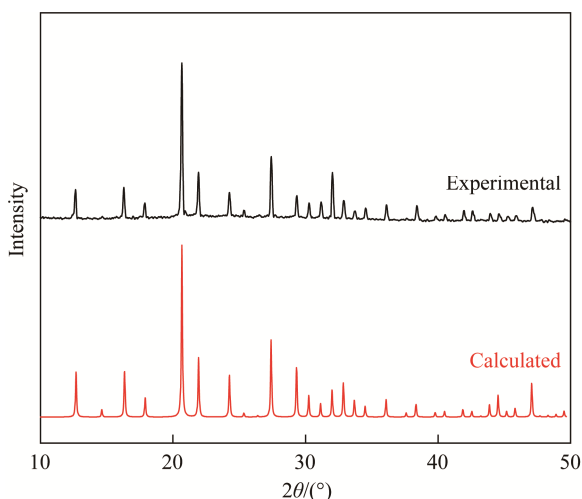
3 Results and discussion

Fig. 4 shows the XRD patterns and IR spectrum of CPA crystal. In Fig. 4(a), the experimental XRD pattern of the as-grown crystals is accordance with the calculated pattern, indicating the good crystallization quality. The two typical morphologies of CPA crystals are pyramid and near hexagonal prism (see Figs. 2a and 2b). The structurally symmetrical pyramid type crystal has an angle of 70.5° between any two adjacent faces except for the underside. For the approximate hexagonal prism type crystals, the neighbor face angle is 109.5° . All these faces belong to the (111) faces and develop completely.

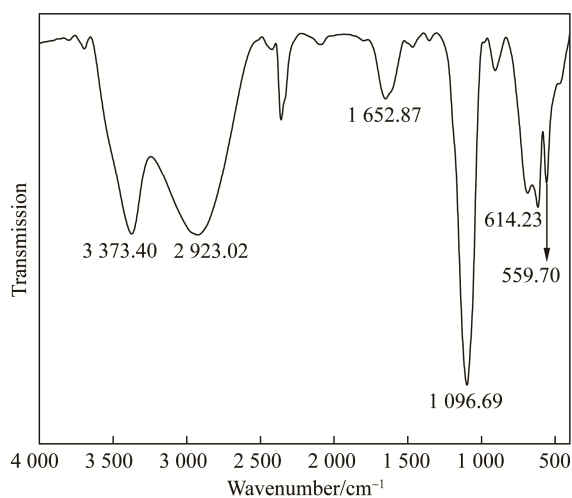
In Fig. 4(b), the absorption peaks at $3\ 373.40\ \text{cm}^{-1}$, $1\ 652.87\ \text{cm}^{-1}$ and $2\ 923.02\ \text{cm}^{-1}$ correspond to the vibrations of H_2O . The absorption peaks at $1\ 096.69\ \text{cm}^{-1}$,

$905.07\ \text{cm}^{-1}$, $614.23\ \text{cm}^{-1}$ and $559.70\ \text{cm}^{-1}$ are due to the fundamental frequency of $[\text{SO}_4]^{2-}$ groups in CPA crystal^[13].

Fig. 5 shows the TG/DSC curves of CPA crystal. Clearly, there are two peaks in the DSC curve. One peak at a low temperature (*i.e.*, 83.8°C) corresponds to the melting point of CPA crystal, which is consistent with the value reported in the literature^[14], and another peak at 167.7°C reflects loss of water. According to the TG curve, the onset dehydration temperature of CPA single crystal is 54.8°C . The mass loss of 18.5% (the calculated value is 18.0%) occurs, which corresponds to the loss of 5 mol H_2O per molar CPA crystal. At 167.7°C , another 5 mol H_2O is lost (the total 37.2% in mass loss), which accords with the calculated mass loss of 36.1%. The mass loss at a higher temperature may originate from the volatilization of sulfur.



(a) XRD patterns of CPA crystal



(b) IR spectrum of CPA crystal

Fig. 4 XRD and IR results of CPA

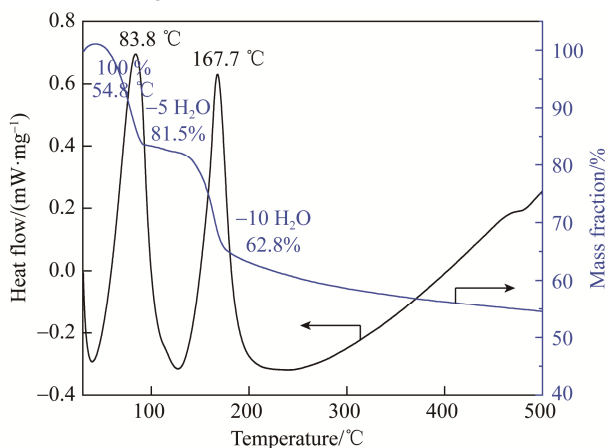


Fig. 5 TG-DSC curves of CPA crystal

Fig. 6(a) shows the temperature (T)-dependent magnetic susceptibility (χ). As is shown by the dash line, $\frac{1}{\chi}-T$ curve is flat, indicating that the CPA crystal is a paramagnetic material according to the

Curie-Weiss law:

$$\chi = C / (T - \theta) \quad (1)$$

where θ is the Weiss constant and C is the Curie constant. The θ was calculated to be 3.31 K, showing the weak ferromagnetic property in CPA crystal at extremely low temperatures, which is propitious to the magnetocaloric effect. The experimental value of C is $2.22 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$.

$$\mu_{\text{eff}} = \sqrt{8C} \mu_B \quad (2)$$

where μ_{eff} is the effective magnetic moment and μ_B is the Bohr magnetic moment. The μ_{eff} was calculated to be $4.21 \mu_B$, which is close to the value for the stable trivalent Cr^{3+} state (*i.e.*, $3.87 \mu_B$). The susceptibility is almost zero at 25 K, which implies the weaker magnetocaloric effect under this condition. Fig. 6(b) shows the magnetization vs magnetic field strength curves measured at 2–10 K. The flatter curves at higher temperatures indicates a lower ferromagnetic field strength.

The magnetocaloric effect can be represented by the isothermal magnetic entropy change ($-\Delta S$) (see Fig. 6(c)), which is calculated from the magnetization data using the Maxwell equation^[15–16]:

$$\begin{aligned} \Delta S(T)_{\Delta H} &= \int_0^H \left[\frac{\partial M(T, H)}{\partial T} \right]_H dH \\ &= \frac{\delta H}{2\delta T} (\delta M_1 + 2 \sum_{k=2}^{n-1} \delta M_k + \delta M_n) \end{aligned} \quad (3)$$

where, temperature (T) can be considered as $T = \frac{T_p + T_q}{2}$ (the integer $p=1-n$, $q=p-1$), and

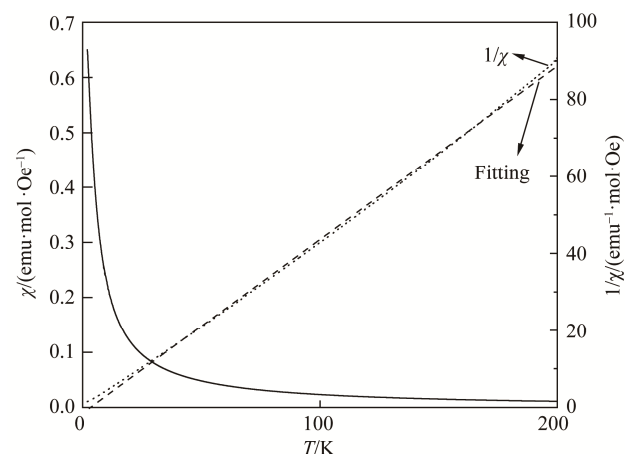
$T = T_p - T_q$ is the temperature difference between the

two sets of isothermal $M-H$ curves. n is the number of points measured for each isotherm. The magnetic field changes from H_1 to H_n at $\delta H = \frac{H_n - H_1}{n-1}$.

The difference in magnetization at T_p and T_q for per step is $\delta M_k = M(T_p)_k - M(T_q)_k$.

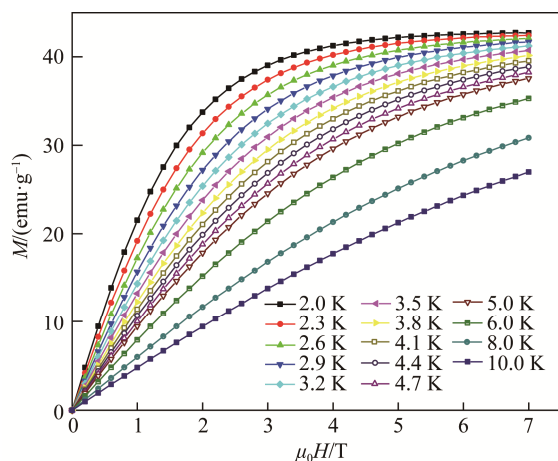
In Fig. 6(c), the isothermal magnetic entropy change $-\Delta S$ is smaller at a higher temperature. At a lower temperature, the magnetocaloric effect of CPA is more intense, and the maximum $-\Delta S$ is up to $29.75 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ at 2 K. These indicate that CPA crystal can be used as a cooling working medium at 2 K.

A CPA salt pill (21.33 g CPA crystals) was produced, in which the crystals grew on a bundle of copper wires with a wire diameter of 0.25 mm and a wire spacing of 1 mm. The salt pill was later used in a two-stage single shot ADR. As $\mu_0 H/T = 2 \text{ T/K}$ and 2 T/300 mK , the salt pill was cooled down to 98 mK and 90 mK through an adiabatic demagnetization process. For comparison, pills in established ADR systems were almost filled of CPA crystal material to achieve an extreme low temperature refrigeration effect.

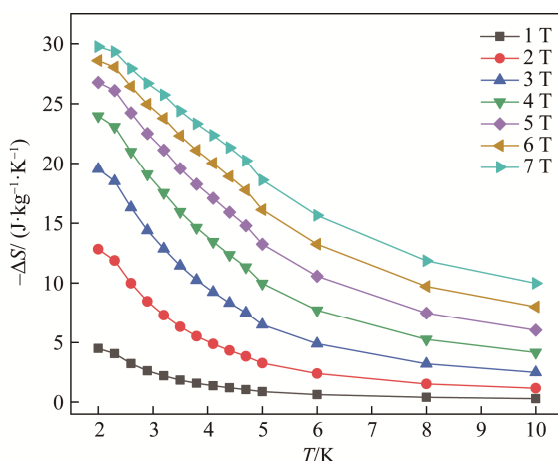


The dash line shows a fitting of the Curie–Weiss law

(a) Susceptibility (χ) temperature (T) and $1/\chi$ - T curves measured at magnetic field strength (H)=30 000 Oe



(b) Magnetization (M) magnetic field strength (H) curves measured at different temperatures



(c) Isothermal magnetic entropy change ($-\Delta S$) temperature (T)

Fig. 6 Results of magnetic properties tests

The CPA pill containing 90 g crystals reported by JAXA^[17] reached 50 mK at 3 T. For three-stage ADR in Astro-H^[18], the CPA stage (270 g CPA crystals) was cooled from 500 mK to 47 mK in a magnetic field of

2 T. In this work, we tried to improve the cooling ability *via* utilizing a small amount of CPA crystals. The soldering quality between the copper wire and extending copper rod is not good, leading to a relatively high cooling temperature.

4 Conclusions

A chromium potassium alum (CPA) single crystal with the size of 32 mm×32 mm×20 mm was grown by a slow-cooling method. The XRD pattern indicates that CPA crystal has a good crystallization. The peaks in the IR spectrum corresponded to different chemical groups of CPA crystal. The TG/DSC curves showed that the melting point of CPA crystal is 83.8 °C. CPA began to lose water at 54.8 °C, and lost 10 mol H₂O per molar CPA crystal at 167.7 °C. The two typical morphologies of CPA crystals were pyramid and near hexagonal prism. The maximum isothermal magnetic entropy change $-\Delta S$ of CPA crystal was 29.75 J·kg⁻¹·K⁻¹ at 2 K in a magnetic field of 7 T. A salt device containing 21.33 g CPA was obtained under the same condition as the growth of single crystal. In the ADR system, the device reached 90 mK from 300 mK at an applied magnetic field of 2 T. Based on this work, we would focus on the fabrication of CPA salt pills used in a magnetic adiabatic refrigerator. The improvement on the thermal bus configuration was still needed.

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