Large Magnetic-Field-Induced Strains in Sintered Chromium Tellurides

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Sintered samples of Cr1Te4 and Cr2Te3 are found to show large strains accompanied by large volume changes under a magnetic field. In Cr1Te4, volume increases of ΔV/V = 500–1170 ppm by applying a magnetic field of 9 T are observed over the entire temperature range below 350 K. At room temperature, the ΔV/V value exceeds 1000 ppm, which is considerably larger than the maximum values reported for Cr-based magnets thus far and is comparable to the room-temperature value of forced-volume magnetostriction in invar alloys. Cr2Te3 show a large ΔV/V of 680 ppm when applying a magnetic field of 9 T at 200 K. Both samples display particularly large volume increases around the Curie temperature, where they also show negative thermal expansion due to microstructural effects, suggesting that the cooperation between anisotropic lattice deformation associated with the magnetic ordering and microstructural effects is essential for the manifestation of the large magnetic-field-induced volume changes.

The strain that magnetic materials experience when a magnetic field is applied has long been the subject of research. The magnetostriction of iron and nickel, which show linear strains of several tens of ppm, is the most classical example. Subsequent studies have led to the development of giant magnetostrictive materials, such as Terfenol-D, which can realize large magnetostrictions exceeding 2000 ppm. Such materials have been put into practical use as ultrasonic transducers and actuators. The strains in the ferromagnetic metals mentioned above are caused by the alignment of ferromagnetic domains in magnetic fields and are therefore essentially directional with little volume changes and are saturated at high magnetic fields where the magnetization saturates. In contrast, invar alloys have displayed large volume changes induced by magnetic fields, known as forced volume magnetostriction. The magnitude of such a change was reported to be ΔV/V = 70 ppm under a magnetic field of 0.5 T at room temperature, which is much larger than the forced volume magnetostrictions in iron and nickel. In invar alloys, large spontaneous magnetostriction caused by the strong magneto-volume effect cancels the thermal expansion due to lattice vibrations, resulting in low thermal expansion. This strong magneto-volume effect also plays a major role in the emergence of large volume changes under magnetic fields.

In recent years, magnetic-field-induced strains accompanied by large volume changes have been discovered in several Cr-based magnets, which have been infrequently thought of as candidate magnetostrictive materials. Large volume increases reaching ΔV/V = 700 ppm under a magnetic field of 9 T were observed in LiInCr4S8 just below the Néel temperature of TN = 24 K and in AgCrS2 at TN = 42 K. These volume increases are smaller than those in invar alloys, but remain reasonably large. ZnCr2Se4 and Cr2Te3 have also been reported to exhibit large linear strains in magnetic fields, although it is unclear whether they are accompanied by volume changes. Most of these Cr-based magnets are antiferromagnetic insulators, unlike invar alloys, suggesting that the large magnetic-field-induced volume changes in Cr-based magnets are caused by a new mechanism based on the characteristic features of Cr spins, such as magnetic ordering accompanied by structural distortion, strong spin-lattice coupling, and geometrical frustration. Therefore, further studies on the magnetostructural properties of Cr-based magnets are expected to lead to the emergence of novel correlated phenomena between their magnetism and volume. In addition, in Cr-based magnets, the large volume changes are realized in a narrow temperature window far below room temperature, because the magnetic phase transition plays an essential role. Therefore, if we use them as magnetostrictive materials, they are only available for limited applications.

In this letter, we focus on the magnetic-field-induced strain in Cr-Te binary compounds, namely, Cr1Te4 and Cr2Te3. As shown in Fig. 1(a), both compounds crystallize in the NiAs-based crystal structures, where the metal atoms form a primitive hexagonal structure with stacked triangular lattices. In Cr1Te4 and Cr2Te3, completely occupied Cr layers and Cr deficient layers with Cr vacancies stack alternately. In Cr1Te4,
the Cr atoms are linearly aligned in a Cr-deficient layer, resulting in monoclinic C2/m symmetry.10,11 In contrast, Cr$_2$Te$_3$ has a honeycomb-type order made of Cr atoms and vacancies in a Cr-deficient layer, resulting in trigonal P 31c symmetry.12 Cr$_3$Te$_4$ and Cr$_2$Te$_3$ were reported to be metallic ferromagnets with Curie temperatures of $T_C = 320$ and 180 K, respectively.11-14

Recently, Cr-Te binary compounds, including Cr$_3$Te$_4$ and Cr$_2$Te$_3$, have been intensively studied from the perspective of room-temperature ferromagnets with tunable $T_C$ values.15-17 However, they are not simple ferromagnets. The magnetization of Cr$_3$Te$_4$ slightly decreases at $T_i = 80$ K, far below $T_C$, when the temperature is decreased in a low magnetic field. This decrease was proposed to be due to the change in spin structure from ferromagnetic to canting antiferromagnetic.12,18,19 In Cr$_2$Te$_3$, neutron scattering data suggests that the Cr spin moment in the Cr deficient layers is negligibly small and opposite to the direction of the net magnetic moment.12,20 For the emergence of these complex magnetic properties, the coexistence of ferromagnetic and antiferromagnetic interactions in Cr-based magnets and the presence of the Cr-deficient layers are likely to be important. There has only been one previous study on the strains in different from the magneto-volume effect present in invar alloys. Discussions based on the experimental data of the volume changes in magnetic fields, the temperature dependence of magnetization, and the thermal expansion suggest that the large magnetic-field-induced volume changes in both compounds are caused by a unique mechanism in which anisotropic lattice deformation and microstructural effects might play a role, which is different from the magneto-volume effect present in invar alloys.

Sintered samples of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ were synthesized by a solid-state reaction method. Stoichiometric amounts of Cr and Te powders were mixed, pressed into pellets, and then sealed in an evacuated quartz tube. The tube was heated to and kept at 873 K for 12 h and then 1273 K for 48 h. The obtained polycrystalline samples were pulverized and sintered at 1073 K for 5 min using a spark plasma sintering furnace (SPS Syntex). Sample characterization was performed by powder X-ray diffraction (XRD) analysis with Cu Kα radiation at room temperature using a MiniFlex diffractometer (RIGAKU), confirming that the single-phase samples of Cr$_3$Te$_4$ and Cr$_2$Te$_3$, with the same crystal structures as in previous studies, were obtained (Supplementary Fig. 1).10,12 The linear strain in magnetic fields and linear thermal expansion of the sintered samples were measured using a strain gage (KFLB, 120W, Kyowa Electronic Instruments Co.) with a Cu reference.21 The temperature control and application of the magnetic fields were achieved using a Physical Property Measurement System (Quantum Design). A part of the linear thermal expansion data was measured using a laser-interference dilatometer (LIX-2, Ulvac). In the isotropic situation, such as in the sintered sample, a volume change $\Delta V/V$ in a magnetic field, $H$, is represented as $\Delta V/V = 2(\Delta L/L)_x + (\Delta L/L)_y$, where $(\Delta L/L)_x$ and $(\Delta L/L)_y$ are the linear strains measured perpendicular and parallel to $H$, respectively. In the linear thermal expansion measurements of the isotropic samples, $\Delta V/V$ and $\Delta L/L$ have a relationship of $\Delta V/V = 3(\Delta L/L)$. Magnetization was measured using a Magnetic Property Measurement System (Quantum Design). As shown in Fig. 1(b), the synthesized Cr$_3$Te$_4$ and Cr$_2$Te$_3$ samples show ferromagnetic transitions at $T_C = 330$ and 190 K, respectively. The former also shows a slight decrease of magnetization at $T_i = 80$ K. Powder XRD patterns of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ at various temperatures were measured using a SmartLab diffractometer (RIGAKU) with Cu Ka radiation, which was monochromated by a Ge(111)-Johansson-type monochromator.

Figures 2(a) and (c) show the linear strains, $(\Delta L/L)_x$ and $(\Delta L/L)_y$, of the sintered samples of Cr$_3$Te$_4$ and Cr$_2$Te$_3$, respectively. First, the $(\Delta L/L)_x$ of Cr$_3$Te$_4$, shown in the left
As shown in Fig. 3(a), the volume changes of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ sintered samples by applying a magnetic field of 9 T, estimated using the linear strain data shown in Fig. 2. 
(b) Linear thermal expansion of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ sintered samples normalized to 500 K. (c) Temperature dependence of unit cell volumes of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ sintered samples estimated using powder XRD data. In (c), the left and right axes show the data for Cr$_3$Te$_4$ and Cr$_2$Te$_3$, respectively.

In contrast, (ΔL/L)$_{\text{aniso}}$ shows small values of several tens of ppm or less, which are normal values for a ferromagnet.

The linear strains of Cr$_3$Te$_4$ under the magnetic fields, shown in Fig. 2(c), are almost isotropic, i.e., (ΔL/L)$_{\perp}$ (ΔL/L)$_{\parallel}$, unlike those of Cr$_3$Te$_4$. This means that (ΔL/L)$_{\text{aniso}}$ in Cr$_2$Te$_3$ is negligibly small and most ΔL/L values consist of (ΔL/L)$_{\text{aniso}}$ accompanying the volume change. As shown in Fig. 3(a), the ΔV/V under the magnetic field of 9 T was a large value of 680 ppm at 200 K.

The observed magnetic-field-induced volume changes in the sintered samples of both Cr tellurides are reasonably large. In particular, the volume increases of ΔV/V = 1170 ppm at 50 K and ΔV/V = 1070 ppm at 350 K in Cr$_3$Te$_4$ under the magnetic field of 9 T are much larger than the maximum values of 780 and 730 ppm in LiInCr$_2$S$_4$ (22 K) and AgCrS$_2$ (42 K), respectively. The maximum value of ΔV/V = 680 ppm for Cr$_2$Te$_3$ under 9 T at 200 K is also comparable to these values. More importantly, all of the large volume changes in Cr-based magnets reported thus far appeared at low
temperatures. However, Cr$_3$Te$_4$ shows large volume changes over a wide temperature region including room temperature. It is notable that a magnetic field of 9 T induced a significant volume change over 1000 ppm at room temperature and that the volume changes over 500 ppm occurred throughout the entire temperature range below 350 K.

We now discuss the mechanism of the large magnetic-field-induced strains accompanied by a large volume change in Cr$_3$Te$_4$ and Cr$_2$Te$_3$. As can be seen in Fig. 3(a), both materials show a particularly large $\Delta V/V$ near $T_C$, suggesting that the formation of long-range magnetic order is involved in the magnetic-field-induced volume change, same as in LiInCr$_2$S$_3$ and AgCrS$_2$.$^{12}$ However, in these Cr sulfides, large $\Delta V/V$ values only appeared in a very narrow temperature range of several K near $T_N$, whereas Cr$_3$Te$_4$ and Cr$_2$Te$_3$ showed large volume changes over a wide temperature range. In LiInCr$_2$S$_3$ and AgCrS$_2$, there is a discontinuous volume change at $T_N$ and the large magnetic-field-induced volume change is a consequence of a magnetic field effect on the phase transition at $T_N$. As shown in Fig. 3(b), the thermal expansion data of Cr$_3$Te$_4$ and Cr$_2$Te$_3$ also show large volume changes related to the magnetic ordering at $T_C$. However, the volume changes in Cr tellurides were gradual, unlike these sulfides, and appeared as negative thermal expansion. Cr$_3$Te$_4$ shows $\Delta V/V = -1080$ ppm from 120 to 330 K and Cr$_2$Te$_3$ shows $\Delta V/V = -3900$ ppm from 80 to 270 K with increasing temperature. In these temperature regions, the ferromagnetic order is not fully developed due to thermal fluctuations. Therefore, the application of magnetic fields facilitates the ferromagnetic order accompanied by the large volume increase, giving rise to a large volume increase induced by magnetic fields.

An important feature of the negative thermal expansion in Cr tellurides is the fact that the volume change in the dilatometric data does not match the crystallographic volume change determined by the diffraction experiments. As shown in Supplementary Fig. 3, the lattice constant $a$ of Cr$_3$Te$_4$ simply decreases with decreasing temperature from 300 K, whereas $b$ and $c$ increase above 125 K. As a result, the unit cell volume $V$ of Cr$_3$Te$_4$ shown in Fig. 3(c) is almost constant above 125 K and $dv/dT > 0$ below 125 K. In the case of Cr$_2$Te$_3$, $c$ decreases and $a$ increases with decreasing temperature, resulting in the gradual decrease of $V$. Thus, neither material has a temperature region with $dv/dT < 0$, consistent with previous studies.$^{22,23}$ Therefore, the negative thermal expansions in the dilatometric data shown in Fig. 3(b) are most likely due to microstructural effects, appearing in the sintered samples that exhibit anisotropic temperature dependence regarding their lattice constants.$^{24,26}$ The fact that the large magnetic-field-induced volume change and negative thermal expansion have the same origin of the volume change at the ferromagnetic order, strongly suggests that microstructural effects play an important role in the emergence of the large magnetic-field-induced volume change.

In contrast to the negative thermal expansion, to our knowledge, the magnetic-field-induced volume change due to microstructural effects has not been reported thus far. For negative thermal expansion due to microstructural effects, the presence of a direction along which the length of the unit cell shrinks with increasing temperature is essential ($b$ and $c$ axes for Cr$_3$Te$_4$ and $a$ axis for Cr$_2$Te$_3$).$^{25,26}$ Even when the crystallographic unit-cell volume exhibits positive thermal expansion, strong microstructural effect could realize negative thermal expansion in sintered samples.$^{27,28}$ Therefore, the emergence of negative thermal expansion in the temperature region with $dv/dT \geq 0$ in Cr$_3$Te$_4$ and Cr$_2$Te$_3$ suggests that strong microstructural effects are exhibited in these materials, implying that they could also be involved in the large magnetic-field-induced volume change. This is a different mechanism from the strong magneto-volume effect for invar alloys. The volume change by the microstructural effect can be strong against the repeated operation cycles and can also be effective in the fine particles,$^{29}$ suggesting that Cr tellurides are expected to be available as a magnetostrictive material.

Finally, we discuss the large $\Delta V/V$ that appears at 50 K in the Cr$_3$Te$_4$ data, which is probably related to the magnetic structure change at $T_1 = 80$ K.$^{12,18,19}$ As shown in Fig. 3(b), Cr$_3$Te$_4$ shows large positive thermal expansion with the volume change of $\Delta V/V = 3000$ ppm at 50–80 K, indicating that the volume of the ferromagnetic phase at high temperatures is considerably larger than the canted antiferromagnetic phase at low temperatures. As in the case of the ferromagnetic transition at $T_C$, discussed above, the ferromagnetic state might become more stable than the canted antiferromagnetic state by applying a magnetic field, probably resulting in the considerable volume increase. However, the positive thermal expansion at 50–80 K also appear in the unit-cell volume, as shown in Fig. 3(c), suggesting that microstructural effects may not be involved in the large magnetic-field-induced volume change at 50–80 K. The large magnetic-field-induced volume change associated with the change of magnetic structure is similar to that in LiFeCr$_3$O$_8$, which exhibits a spin transition from ferrimagnetic to conical,$^{10}$ but the observed $\Delta V/V$ in Cr$_3$Te$_4$ at 50 K is more than double the maximum value in LiFeCr$_3$O$_8$.

In summary, the Cr$_3$Te$_4$ and Cr$_2$Te$_3$ sintered samples were found to show large strains accompanied by large volume increases in magnetic fields. The observed maximum volume increase under a magnetic field of 9 T is $\Delta V/V = 1170$ and 680 ppm for Cr$_3$Te$_4$ and Cr$_2$Te$_3$, respectively. In particular, Cr$_3$Te$_4$ exhibited $\Delta V/V > 1000$ ppm at room temperature, which is comparable to the forced volume magnetostriction in invar alloys. Both the Cr$_3$Te$_4$ and Cr$_2$Te$_3$ samples showed a particularly large magnetic-field-induced volume change at around $T_C$ and negative thermal expansion caused by microstructural effects. The cooperation of anisotropic lattice
deformation at the magnetic order and microstructural effects, which is in contrast to the magneto-volume effect operative in invar alloys, is most likely responsible for the large magnetic-field-induced volume changes in the Cr tellurides. This is a novel magneto-volume phenomenon occurring in Cr-based magnets.

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1A. E. Clark, J. P. Teter, and O. D. McMasters, J. Appl. Phys. 63, 3910 (1988).

2For a review, see E. F. Wasserman, in Ferromagnetic Materials, vol. 5, edited by K. H. J. Buschow and E. P. Wohlfarth (Elsevier Science Publishing, 1990) pp. 237-322.

3M. Matsumoto, T. Kaneko, and H. Fujimori, J. Phys. Soc. Jpn. 26, 1083 (1969).

4T. Kanematsu, M. Mori, Y. Okamoto, T. Yajima, and K. Takenaka, J. Phys. Soc. Jpn. 89, 073708 (2020).

5T. Kanematsu, Y. Okamoto, and K. Takenaka, Appl. Phys. Lett. 118, 142404 (2021).

6J. Hemberger, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. 98, 147203 (2007).

7Z. Z. Jiang, X. Liang, X. Luo, J. J. Gao, W. Wang, T. Y. Wang, X. C. Yang, X. L. Wang, L. Zhang, Y. Sun, P. Tong, J. F. Hu, W. H. Song, W. J. Lu, and Y. P. Sun, Phys. Rev. B 106, 094407 (2022).

8Y. Okamoto, M. Mori, N. Katayama, A. Miyake, M. Tokunaga, A. Matsuo, K. Kindo, and K. Takenaka, J. Phys. Soc. Jpn. 87, 034709 (2018).

9P. F. Bongers, C. F. Van Bruggen, J. Koopstra, W. P. F. A. M. Omloo, G. A. Wiegers, and F. Jellinek, J. Phys. Chem. Solids 29, 977 (1968).

10M. Chevreton and G. Berodias, Comptes Rendus Hebdomadaires des Seances de l’Academie des Sciences 261, 1251-1254 (1965).

11E. F. Bertaut, G. Roult, R. Aleonard, R. Pauthenet, M. Chevreton, and R. Jansen, J. Phys. (Paris) 25, 582 (1964).

12A. F. Andresen, Acta Chemica Scandinavica 24, 3495 (1970).

13E. Gronvold and E. F. Westrum Jr., Z. anorg. allg. Chem. 328, 272 (1964).

14K. Ozawa, S. Yanagisawa, T. Yoshimi, M. Ogawa, and S. Anzai, phys. stat. sol. 38, 385 (1970).

15X. Zhang, B. Wang, Y. Guo, Y. Zhang, Y. Chen, and J. Wang, Nanoscale Horiz. 4, 859 (2019).

16Y. Wen, Z. Liu, Y. Zhang, C. Xia, B. Zhai, X. Zhang, G. Zhai, C. Shen, P. He, R. Cheng, L. Yin, Y. Yao, M. G. Sendaeki, Z. Wang, X. Ye, C. Liu, C. Jiang, C. Shan, Y. Long, and J. He, Nano Lett. 20, 3130 (2020).

17L.-Z. Zhang, X.-D He, A.-L. Zhang, Q.-L. Xiao, W.-L. Lu, F. Chen, Z. Feng, S. Cao, J. Zhang, and J.-Y. Ge, APL Mater. 8, 031101 (2020).

18M. Yamaguchi and T. Hashimoto, J. Phys. Soc. Jpn. 32, 635 (1972).

19S. Ohta, J. Phys. Soc. Jpn. 54, 1076 (1985).

20T. Hamasaki and T. Hashimoto, Solid State Commun. 16, 895 (1975).

21K. Takenaka, M. Ichida, T. Hamada, A. Ozawa, T. Shibayama, T. Inagaki, and K. Asano, Sci. Technol. Adv. Mater. 15, 015009 (2014).

22S. Ohta, T. Kaneko, H. Yoshida, J. Magn. Magn. Mater. 163, 117 (1996).

23S. Ohta, Y. Adachi, T. Kaneko, M. Yuzuri, and H. Yoshida, J. Phys. Soc. Jpn. 63, 2225 (1994).

24F. H. Gillery and E. A. Bush, J. Am. Ceram. Soc. 42, 175 (1959).

25K. Takenaka, Y. Okamoto, T. Shinoda, N. Katayama, and Y. Sakai, Nat. Commun. 8, 14102 (2017).

26N. Katayama, K. Otsuka, M. Mitamura, Y. Yokoyama, Y. Okamoto, and K. Takenaka, Appl. Phys. Lett. 113, 181902 (2018).

27A. Doi, S. Shimano, T. Matsunaga, Y. Tokura, and Y. Taguchi, Appl. Phys. Express 14, 107001 (2021).

28Y. Kadowaki, R. Kasugai, Y. Yokoyama, N. Katayama, Y. Okamoto, and K. Takenaka, Appl. Phys. Lett. 119, 171901 (2021).

29K. Takenaka, M. Sato, M. Mitamura, Y. Yokoyama, N. Katayama, and Y. Okamoto, J. Am. Ceram. Soc. 103, 2757 (2020).

30Y. Okamoto, T. Kanematsu, Y. Kubota, T. Yajima, and K. Takenaka, J. Phys. Soc. Jpn. 91, 023710 (2022).
Supplementary Note 1. Powder X-ray diffraction patterns of Cr₃Te₄ and Cr₂Te₃

Supplementary Fig. 1 shows the powder X-ray diffraction (XRD) patterns of the sintered samples of Cr₃Te₄ and Cr₂Te₃ measured at room temperature. All diffraction peaks in the Cr₃Te₄ data were indexed on the basis of monoclinic C2/m symmetry, while those in the Cr₂Te₃ data were indexed on the basis of trigonal P 31c symmetry, indicating that the single-phase samples of Cr₃Te₄ and Cr₂Te₃ with the same crystal structures as in previous studies were obtained.¹⁰,¹²

Supplementary Fig. 1. Powder XRD patterns of sintered samples of Cr₃Te₄ and Cr₂Te₃ measured at room temperature. Peak indices for the Cr₃Te₄ data are given using a monoclinic unit cell with lattice constants of a = 13.9846 Å, b = 3.933 Å, and c = 6.8658 Å, and b = 118.302°, and those for Cr₂Te₃ are given using trigonal one with those of a = 6.7986 Å and c = 12.1076 Å.

Supplementary Note 2. Magnetization process of Cr₃Te₄ sintered sample

Supplementary Fig. 2 shows the magnetization process of the Cr₃Te₄ sintered sample measured at 5, 50, 150, and 300 K. Magnetization measurements were performed using a Magnetic Property Measurement System (Quantum Design). All the data showed concave downward behavior, reflecting the presence of a ferromagnetic moment below \( T_C \approx 330 \text{ K} \). The difference of the saturation field between 150 and 50 K might be due to the magnetic structure change at \( T_C \).

Supplementary Fig. 2. Magnetization curves of Cr₃Te₄ sintered samples measured at 5, 50, 150, and 300 K.

Supplementary Note 3. Temperature dependences of lattice constants of Cr₃Te₄ and Cr₂Te₃

Supplementary Fig. 3 shows the temperature dependences of the lattice constants determined by XRD data of the sintered samples of Cr₃Te₄ (a, b) and Cr₂Te₃ (c, d). In Cr₃Te₄, with decreasing temperature from 300 to 125 K, \( a \) decreases while \( b \) and \( c \) increase, resulting in the almost constant unit cell volume \( v \) above 125 K, as shown in Fig. 3(c). In Cr₂Te₃, \( c \) decreases while \( a \) increases with decreasing temperature in all the measured temperature range below 300 K, resulting in the gradual decrease of \( v \), as shown in Fig. 3(c).

Supplementary Fig. 3. Temperature dependences of lattice constants determined by powder XRD measurements on Cr₃Te₄ (a, b) and Cr₂Te₃ (c, d) sintered samples. In (a) and (b), the left axis shows \( a \) and \( c \), while the right axis shows \( b \) and \( b \), respectively.