Al-doping-induced magnetocapacitance in the multiferroic $CuCrS_2$*

Liu Rong-Deng(刘荣灯)[a)b)], Liu Yun-Tao(刘蕴韬)[a)], Chen Dong-Feng(陈东风)[a)], He Lun-Hua(何伦华)[b)], Yan Li-Qin(闫丽琴)[b)], Wang Zhi-Cui(王志翠)[b)], Sun Yang(孙 阳)[b)], and Wang Fang-Wei(王芳卫)[b)†]

[a)] *China Institute of Atomic Energy, Beijing* 102413, *China*

[b)] *State Key Laboratory of Magnetism, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

(Received 14 May 2012; revised manuscript received 6 September 2012)

In this paper, magnetic and dielectric properties of the quasi-two-dimensional triangular-lattice system $CuCrS_2$ and its B-site-diluted analogs $CuAl_{1-x}Cr_xS_2$ ($x = 0.01$ and $x = 0.02$) are investigated. Antiferromagnetic phase transition is observed at about 38.5 K by magnetization measurement without shift induced by a small amount of doping Al. Magnetodielectric effect is found near T_N in each of the three compounds. The dielectric constant decreases and the magnetocapacitance increases with the increase of substitution of nonmagnetic Al^{3+} ions for the magnetic Cr^{3+} ions. The negative magnetocapacitive effect reaches $\sim 13\%$ for $CuAl_{0.02}Cr_{0.98}S_2$.

Keywords: magnetocapacitance, dielectric property, magnetoelectric coupling, antiferromagnetics

PACS: 75.80.+q, 77.22.–d, 75.85.+t, 75.50.Ee **DOI:** 10.1088/1674-1056/22/2/027507

1. Introduction

In recent years, interest has been aroused in the correlation between magnetic and dielectric properties, not only for fundamental scientific research, but also for practical application in materials-engineering.[1–7] Toward the enhanced magnetoelectric coupling, the multiferroic materials with dielectric and magnetic orders have been extensively explored, but the attempts have not been fully successful. For example, some materials even with the multiferroic orders, exhibit magnetic and dielectric phase transitions at various temperatures, resulting in the weak coupling between the orders. As the helimagnetic ferroelectric material ABX_2 family with the delafossite structure (A=nonmagnetic monovalent ion, B=magnetic trivalent ion, and X=bivalent anion) has been discovered, the mutual manipulation of the magnetic and dielectric properties becomes possible.[3,8–12]

$CuCrS_2$, which is interesting and important in science and industry, has been extensively investigated.[13–17] At room temperature, it crystallizes into space group $R3m$ with a quasi-two-dimensional layered structure. The basic crystal structure is composed of covalent-ionic bound S–Cr–S trilayers which are separated by a van der Waals gap and weakly coupled. The unit of CrS_2 is metastable and comes into being only with an electron donor, hereby the univalent ions Cu^+ are sandwiched between CrS_2 as shown in Fig. 1(a). At 300 K, $CuCrS_2$ exhibits a paramagnetic electron–ion semiconducting behavior and it undergoes the super-ionic conductor–semiconductor transition and the electronic transition at 675 K and 110 K, respectively. At about 37 K, it experiences the paramagnet–antiferromagnet and the semiconductor–insulator transitions. In the past several years, $CuCrS_2$ has been an intensively interesting subject as a multiferroic material due to the discovery of spontaneous electric polarization in the corresponding $CuCrO_2$ oxide.[3,8,18] In the present paper, we report that the magnetic defects caused by only a few percent dilution of the magnetic ions Cr^{3+} with the nonmagnetic ions Al^{3+} induce the negative magneto-capacitive effect.

2. Experiment

The polycrystalline samples of $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) were prepared by the standard solid-state synthesis method. High-purity powders of copper (I) sulfide (Cu_2S), chromium (III) sulfide (Cr_2S_3), and aluminum sulfide (Al_2S_3) precursors were weighted according to the relevant stoichiometric ratios. The resulting powders were carefully ground, pelletized, and sealed into an evacuated quartz tube. The tube was heated at 1125 K for 50 h. At room temperature, the phase composition and the structure of the annealed samples were characterized by powder X-ray diffraction (XRD), using a type RINT 2400 diffractometer (Rigaku Corporation) with graphite monochromatized Cu Kα radiation.

The direct-current (DC) magnetic susceptibilities were measured under an applied magnetic field of 0.1 T in a temperature range of 3 K–400 K by using a Squid magnetometer (Quantum Design, MPMSXL-7).

For the dielectric measurements, the samples were cut into three thin plates each with a size of about 3 mm×5 mm×0.4 mm, and the electrodes were formed on

*Project supported by the National Basic Research Program of China (Grant No. 2010CB833102) and the National Natural Science Foundation of China (Grant No. 10974244).

†Corresponding author. E-mail: fwwang@aphy.iphy.ac.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

both sides of the plates by heat-treated silver paste. The dielectric measurements were performed on a Hioki-3532-50 LCR meter at a frequency of 1 MHz. The controls of the sample temperature and the external magnetic field were ensured by the Squid magnetometer. The direction of the electric field was perpendicular to the magnetic field in all dielectric measurements.

3. Results and discussion

Figure 1(b) shows the XRD patterns of $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) samples at room temperature, confirming that all the samples exhibit single-phase characteristics within the detection limit of XRD. Comparing the patterns with the patterns expected for randomly oriented crystallites of $CuCrS_2$, we find that the increased intensities of all the (001) reflections show that all the samples have some preferred orientations. All the diffraction peaks can be indexed by using the Joint Committee on Powder Diffraction Standards Card (the card: 83-1690) for rhombohedral acentric *R*3*m* $CuCrS_2$,[8,15,17] indicating that there are crystal structures with little remaining Al doping. The radius ratio of nonmagnetic ion Al^{3+} to magnetic ion Cr^{3+} is 0.81, higher than 0.59: the criterion of the ratio of the ionic radius of the solute to that of the solvent of forming interstitial solid solution.[19] So, Al^{3+} ions must replace Cr^{3+} ions in the compound of $CuCrS_2$. The substitution of a few percent Al^{3+} for Cr^{3+} cannot make the XRD patterns evidently different.

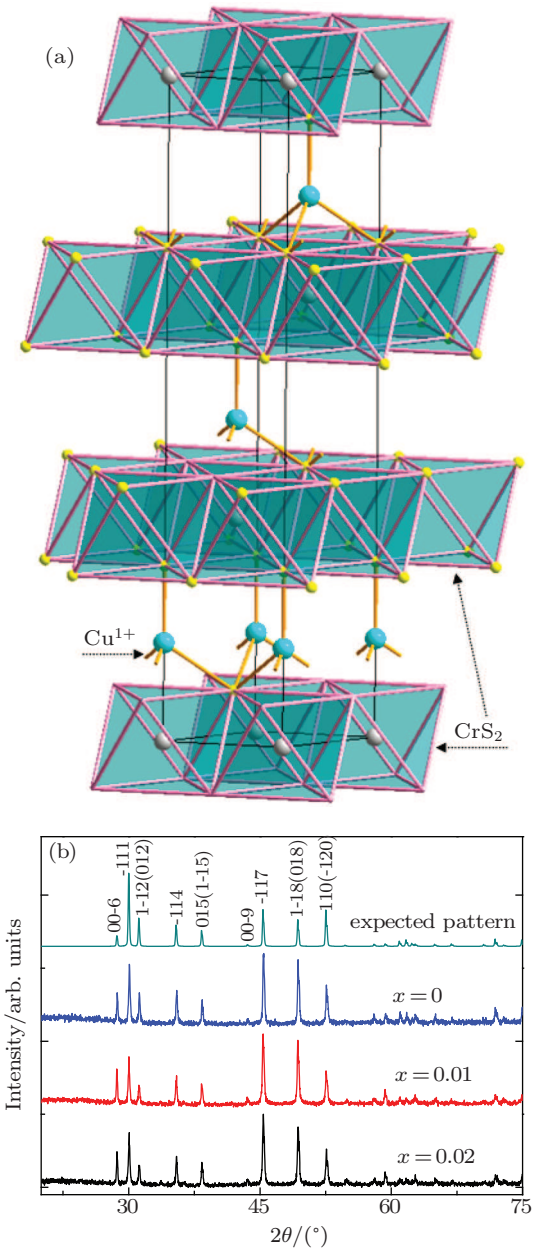


Fig. 1. (color online) (a) Crystalline structure of $CuCrS_2$, and (b) X-ray diffraction patterns of the $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) samples and expected pattern of $CuCrS_2$.

Figure 2 displays the temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities and the corresponding reciprocal magnetic susceptibilities under an applied magnetic field of 0.1 T. The antiferromagnetic transitions are observed at about 38.5 K, which is consistent with the previously reported results[8,13,15,16] but larger than those reported for the corresponding $CuCrO_2$ oxide[3,9,18] ($T_N = 23$ K). The Néel temperature T_N is not obviously changed by a few substitutions of Al^{3+} for Cr^{3+} in the compound of $CuCrS_2$. We fit the data from 150 K to 400 K to the Curie–Weiss law, obtaining the effective Bohr magnetons and the Weiss temperatures. The values of Cr^{3+} effective Bohr magnetons are 3.82 μ_B, 3.77 μ_B, and 3.78 μ_B, respectively, consistent with the expected value (3.87 μ_B) of the Cr^{3+} ion and previous experimental results.[8,13,15,17] The Weiss temperatures are −141.45 K, −129.27 K, and −140.16 K, respectively, which indicate predominantly antiferromagnetic interactions. The frustration parameter values of the specimens ($f = |\theta|/T_N$) are 3.69, 3.38, and 3.64, respectively, which are rather small compared with the value of a strongly frustrated system (usually larger than 10).[20]

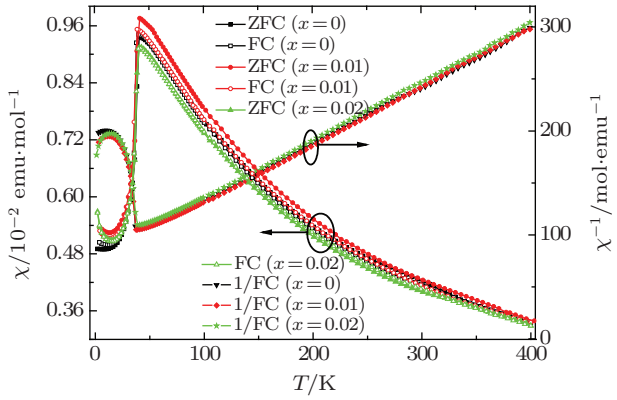


Fig. 2. (color online) Temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities (right scale) and the corresponding reciprocal magnetic susceptibilities (left scale) of $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) measured at 0.1 T.

Figure 3 presents the temperature dependences of the dielectric constants (a) and the dielectric loss tangents (b) in the cases without and with an applied magnetic field of 7 T near the Neel temperature in a range of 25 K to 55 K of the compounds, measured at a frequency of 1 MHz. As the temperature is lowered, the dielectric constants of $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) decrease and reach a local minimum near T_N. Below T_N, the dielectric constants rise in a narrow temperature region and then decrease again with temperature decreasing. These "inverse S-type" behaviors that indicate that magnetoelectric coupling takes place, are very similar to those of polycrystalline $YMnO_3$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$.[21–23] The dielectric constant of $CuCrS_2$ is rather larger than those reported for the corresponding $CuCrO_2$ oxide.[3,9,18] And it reduces sharply with the increase of Al-doping, which is caused by reducing the resistivity due possibly to the Al-doping. In an external field of 7 T, the dielectric constants vary evidently in different samples as illustrated in Fig. 3(a). The magneto-capacitive effect determined the relative difference between the dielectric constant in zero field and that in non-zero field almost reaches -13% for $CuAl_{0.02}Cr_{0.98}S_2$, which must be induced by the magnetic defects resulting in the dilution of the magnetic ions Cr^{3+} with the nonmagnetic ions Al^{3+}. The

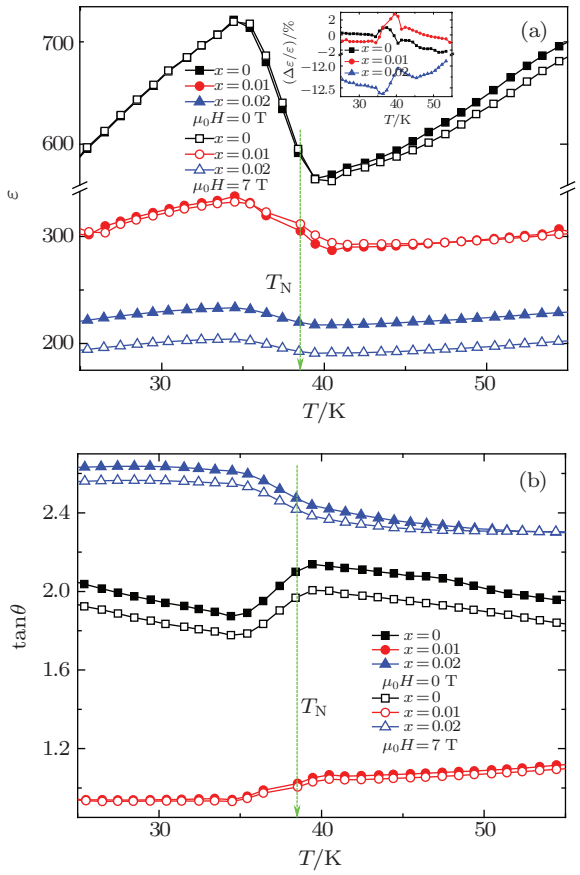


Fig. 3. (color online) Temperature dependences of dielectric constant (a) and dielectric loss tangent (b) in the cases without and with an applied magnetic field of 7 T of $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02), measured at a frequency of 1 MHz. Inset of Fig. 3(a) provides a measure of magneto-capacitance, with $\Delta\varepsilon = \varepsilon(7\text{ T}) - \varepsilon(0\text{ T})$.

existence of the clear dielectric anomaly in each compound is independent of frequency (not shown) and the external magnetic field, which is similar to the result in Ref. [24].

As shown in Fig. 3(b), the dielectric loss tangent anomaly near T_N can also be observed, which is similar to the scenarios of $YMnO_3$, $PbFe_{1/2}Nb_{1/2}O_3$, and $Cd_{0.7}Fe_{0.3}Cr_2S_4$.[21–23] This is a characteristic of multiferroics, and indicates the existence of the magnetodielectric effect. However, unlike the dielectric constant, the dielectric loss tangents of different samples exhibit various tendencies. For the parent compound of $CuCrS_2$, the dielectric loss tangent decreases as the temperature increases in a range below T_N. Near T_N it sharply rises in a narrow temperature region and then decreases again with temperature increasing. With the increase of temperature, the dielectric loss tangent of $CuAl_{0.01}Cr_{0.99}S_2$ increases slowly in the whole temperature region except near T_N. In contrast, the dielectric loss tangent of $CuAl_{0.02}Cr_{0.98}S_2$ decreases slowly in the whole temperature region except near T_N. Similar to the dielectric constant, the existence of the anomaly in each compound is independent of frequency (not shown) and external magnetic field. However, its values are dependent on frequency (not shown) and field. The results indicate that the magnetic defects can modulate the dielectric loss tremendously.

Incidentally, the small dielectric anomaly is observed near the antiferromagnetic transition temperature for each of the samples, which is similar to the previous results. Usually, such an anomaly in dielectric constant may originate from various factors, such as an extrinsic resistive component of the dielectric response together with the Maxwell–Wagner effect[25–27] and intrinsic multiferroic coupling by the magnetoelastic effect.[4,28] Some investigations by neutron scattering technique evidenced a magnetoelastic coupling induced structural transition at T_N.[8] So, the role of the resistive part of the dielectric response must be insignificant.

4. Conclusion

In this paper, the compounds $CuAl_xCr_{1-x}S_2$ ($x = 0$, 0.01, and 0.02) with delafossite structure, synthesized by the convenient solid reaction method, exhibit the antiferromagnetic transitions and dielectric anomalies at about 38.5 K. The magnetic defects, a few nonmagnetic Al^{3+} ions that substitute the magnetic Cr^{3+} ions, have no influence on magnetic transition temperature but change the values of Cr^{3+} effective Bohr magnetons and the Weiss temperatures slightly. We also find that the magnetic defects reduce the dielectric constant, induce the negative magneto-capacitive effect, and tune the dielectric loss. The above results indicate that B-site dilution with nonmagnetic ions is a promising route to design multiferroic materials.

References

[1] Choudhury N, Walizer L, Lisenkov S and Bellaiche L 2011 *Nature* **470** 513

[2] Takagi H and Hwang H Y 2010 *Science* **327** 1601

[3] Kimura K, Nakamura H, Kimura S, Hagiwara M and Kimura T 2009 *Phys. Rev. Lett.* **103** 107201

[4] Spaldin N A and Fiebig M 2005 *Science* **309** 391

[5] Zhang C H, Xu Z, Gao J J, Zhu C J and Yao X 2011 *Chin. Phys.* B **20** 097702

[6] Ding B F and Zhou S Q 2011 *Chin. Phys.* B **20** 127701

[7] Yan L Q, He L H, Wang F W and Shen J 2011 *Chin. Phys.* B **20** 097503

[8] Rasch J C E, Boehm M, Ritter C, Mutka H, Schefer J, Keller L, Abramova G M, Cervellino A and Loffler J F 2009 *Phys. Rev.* B **80** 104431

[9] Luo S J, Wang K F, Li S Z, Dong X W, Yan Z B, Cai H L and Liu J M 2009 *Appl. Phys. Lett.* **94** 172504

[10] Kundys B, Maignan A, Pelloquin D and Simon C 2009 *Solid State Sci.* **11** 1035

[11] Kanetsuki S, Mitsuda S, Nakajima T, Anazawa D, Katori H A and Prokes K 2007 *J. Phys.: Condens. Matter* **19** 145244

[12] Terada N, Mitsuda S and Gukasov A 2006 *Phys. Rev.* B **73** 014419

[13] Abramova G M, Petrakovskiy G A, Vtyurin A N, Rasch J C E, Krylov A S, Gerasimova J V, Velikanov D A, Boehm V M and Sokolov V 2010 *J. Raman Spectrosc.* **41** 1485

[14] Abramova G, Pankrats A, Petrakovskii G, Rasch J C E, Boehm M, Vorotynov A, Tugarinov V, Szumszak R, Bovina A and Vasilev V 2010 *J. Appl. Phys.* **107** 093914

[15] Tsujii N and Kitazawa H 2007 *J. Phys.: Condens. Matter* **19** 145245

[16] Tsujii N, Kitazawa H and Kido G 2006 *Phys. Stat. Sol.* C **3** 2775

[17] Almukhametov R F, Yakshibayev R A, Gabitov E V, Abdullin A R and Kutusheva R M 2003 *Phys. Stat. Sol.* B **236** 29

[18] Seki S, Onose Y and Tokura Y 2008 *Phys. Rev. Lett.* **101** 067204

[19] Beck M, Ellner M and Mittemeijer E J 2001 *Acta Mater.* **49** 985

[20] Greedan J E 2001 *J. Mater. Chem.* **11** 37

[21] Huang Z J, Cao Y, Sun Y Y, Xue Y Y and Chu C W 1997 *Phys. Rev.* B **56** 2623

[22] Yan L Q, Sun Z H, He L H, Shen J, Zhang J and Wang F W 2008 *J. Appl. Phys.* **103** 07E308

[23] Yang Y, Liu J M, Huang H B, Zou W Q, Bao P and Liu Z G 2004 *Phys. Rev.* B **70** 132101

[24] Fan J, Dong X W, Song Y, Wang K F, Liu J M and Jiang X P 2011 *Chin. Phys.* B **20** 027502

[25] Catalan G 2006 *Appl. Phys. Lett.* **88** 102902

[26] Ritus A I, Pronin A V, Volkov A A, Lunkenheimer P, Loidl A, Shcheulin A S and Ryskin A I 2002 *Phys. Rev.* B **65** 165209

[27] Catalan G, Neill D O, Bowman R M and Gregg J M 2000 *Appl. Phys. Lett.* **77** 3078

[28] Schmid H 2008 *J. Phys.: Condens. Matter* **20** 434201