

## Colossal Magnetocapacitance and Colossal Magnetoresistance in $\text{HgCr}_2\text{S}_4$

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We present a detailed study of the dielectric and charge transport properties of the antiferromagnetic cubic spinel  $\text{HgCr}_2\text{S}_4$ . Similar to the findings in ferromagnetic  $\text{CdCr}_2\text{S}_4$ , the dielectric constant of  $\text{HgCr}_2\text{S}_4$  becomes strongly enhanced in the region below 60–80 K, which can be ascribed to polar relaxational dynamics triggered by the onset of ferromagnetic correlations. In addition, the observation of polarization hysteresis curves indicates the development of ferroelectric order below about 70 K. Moreover, our investigations in external magnetic fields up to 5 T reveal the simultaneous occurrence of magnetocapacitance and magnetoresistance of truly colossal magnitudes in this material.

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The detection of colossal magnetoresistance (CMR) in a number of perovskite-related manganites [1] may be the most notable discovery in solid state physics since the high- $T_c$  superconductors. Very recently another “colossal” effect with tremendous prospects for applications attracted considerable attention: in several materials a strong coupling of magnetic and dielectric properties, termed the “magnetocapacitive” or “magnetoelectric” effect, was found [2,3]. Among these, the cubic spinel  $\text{CdCr}_2\text{S}_4$  stands out by showing simultaneous ferromagnetic (FM) and relaxor ferroelectric (FE) behavior [3] and by setting a record value of the magnetocapacitive effect with an increase of the dielectric constant  $\epsilon'$  of up to a factor of 30 in a magnetic field of 10 T [4]. At the FM transition at  $T_c \approx 84$  K,  $\epsilon'$  shows a strong increase, which was ascribed to a speeding up of relaxational dynamics under the formation of magnetic order [4]. However, clearly the microscopic origin of this extraordinary behavior is far from being understood. A similar, but weaker effect was recently reported in isostructural  $\text{CdCr}_2\text{Se}_4$  [5] exhibiting FM order below  $T_c \approx 125$  K. In the present Letter, we provide dielectric data on  $\text{HgCr}_2\text{S}_4$ , which do not show any long-range FM order but exhibit a complex antiferromagnetic (AFM) state [6]. Nevertheless, the data show a colossal magnetocapacitance (CMC) of even larger amplitude than in  $\text{CdCr}_2\text{S}_4$  and, most remarkably, the simultaneous occurrence of CMR. In addition, our experiments indicate that in  $\text{HgCr}_2\text{S}_4$ , similar to  $\text{CdCr}_2\text{S}_4$ , short-range FE order develops at low temperatures.

All measurements were performed on single crystals of  $\text{HgCr}_2\text{S}_4$ , grown by chemical transport. Measurements with silver paint and sputtered gold contacts applied to opposite sides of the samples were performed. Details on crystal preparation and experimental methods are given in Refs. [3,6]. A thorough characterization of the magnetic properties of  $\text{HgCr}_2\text{S}_4$  [6] revealed a complex behavior as exemplified by the temperature- and field-dependent magnetization  $M$  shown in Fig. 1(a).  $M(T)$  [left inset of Fig. 1(a)] shows a peak for small magnetic fields. In

moderate fields it shifts to lower temperatures and a strong upturn of  $M(T)$  below 60 K becomes strongly enhanced. Finally, at fields above 1 T the peak becomes suppressed [6]. In Fig. 1(a) we show the magnetization curves for two temperatures. At 30 K, a hysteresis curve is detected resembling that of soft ferromagnets with a remanent magnetization below the detection limit. At 5 K, a clearly nonlinear behavior is observed for  $H < 5$  kOe indicating a complex magnetic structure. In [6], the  $M(T)$  peak was attributed to the development of a spiral-like AFM state with  $T_N \approx 22$  K and the upturn of  $M(T)$  was ascribed to the onset of FM correlations below about 60 K. Full FM

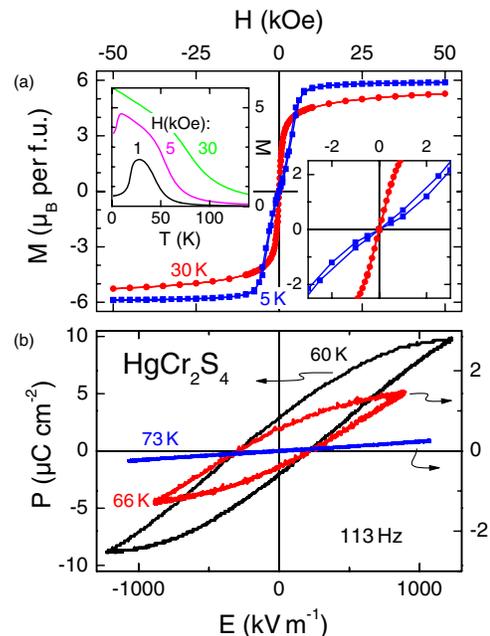


FIG. 1 (color online). (a) Magnetization hysteresis curves for two temperatures. The right inset gives a magnified view for small fields. The left inset shows the temperature-dependent magnetization  $M$  shown in Fig. 1(a).  $M(T)$  [left inset of Fig. 1(a)] shows a peak for small magnetic fields. In

order was stated for fields above 1 T. In contrast, in [7,8] where a continuous field-induced change from the AFM to a FM state due to the tilting of the spiral was reported, a  $T_N$  of about 60 K was deduced from neutron and optical studies. Obviously, the true nature of the magnetic state of  $\text{HgCr}_2\text{S}_4$  still needs some clarification.

To check for possible FE correlations [3], electric polarization cycles were performed. Below about 70 K indeed hysteresis loops show up, becoming more pronounced with decreasing temperature [Fig. 1(b)]. This indicates FE behavior, the absolute values of the polarization  $P$  being significantly higher than in  $\text{CdCr}_2\text{S}_4$  [3]. It was noted in [9] that FE-like hysteresis loops can also arise from nonintrinsic effects. Within this scenario, a decrease of  $P$  with increasing frequency was predicted. Indeed such a behavior is observed in  $\text{HgCr}_2\text{S}_4$  for frequencies between 1 Hz and 1 kHz (not shown). However, this effect can be ascribed to the intrinsic relaxational behavior documented in Fig. 2 (see discussion below) as the dipoles cannot follow the field for higher frequencies [10]. In [9], a second criterion for nonintrinsic behavior was given, namely, the disappearance of the polarization saturation at high frequencies, which clearly is not fulfilled in  $\text{HgCr}_2\text{S}_4$ . To further corroborate FE ordering in this system, we tried to measure the pyro current in order to obtain information on the temperature-dependent polarization. Unfortunately, these experiments were hampered by the relatively high conductivity of the samples at low temperatures. Overall, while the results of Fig. 1(b) strongly suggest FE ordering

in  $\text{HgCr}_2\text{S}_4$ , for a final proof still further experiments are necessary.

In Fig. 2 the temperature-dependent dielectric constant  $\epsilon'$  [Fig. 2(a)] and the conductivity  $\sigma'$  [Fig. 2(b)] are shown for various frequencies at  $T < 150$  K. With decreasing temperature,  $\epsilon'(T)$  exhibits a pronounced steplike increase in the region between 60 and 80 K, which is followed by a decrease at low temperatures. Concomitantly,  $\sigma'(T)$  reveals peaks at frequencies coinciding with the points of inflection of  $\epsilon'(T)$  [arrows in Fig. 2(b)]. They are superimposed to a frequency independent contribution, observed for the lower frequencies, with a peak at about 25 K, which can be ascribed to dc charge transport. Except for the higher dc contribution, this behavior resembles that reported in  $\text{CdCr}_2\text{S}_4$  [3,4]. However, while in  $\text{CdCr}_2\text{S}_4$  an increase of  $\epsilon'(T)$  by about a factor of 5 was observed, in  $\text{HgCr}_2\text{S}_4$  it extends over nearly two decades reaching values of  $\epsilon'$  as high as 2000. The finding of a strong frequency dependence of the step or peak frequencies indicates a relaxational origin of this phenomenon. For relaxational processes, steps in  $\epsilon'(T)$  and peaks in  $\sigma'(T)$  [or the loss  $\epsilon''(T) \sim \sigma'(T)/\nu$ ] occur when the frequency of the exciting field is equal to the temperature-dependent relaxation rate of the relaxing entities, e.g., reorienting dipoles or charged particles jumping within a double-well potential. Obviously, with decreasing temperature in  $\text{HgCr}_2\text{S}_4$  this condition is fulfilled twice, namely, between 40 K and 70 K and again below about 20 K. In the latter region, the peak temperature decreases with decreasing frequency, mirroring the slowing down of the relaxational dynamics for low temperatures. However, between 40 K and 70 K the peaks shift in an opposite way, which, in line with the interpretation of the results in  $\text{CdCr}_2\text{S}_4$  [4], indicates an unusual *acceleration* of the dynamics with decreasing temperature. It is this increase of the relaxational mobility that leads to the strong upturn of  $\epsilon'$  below about 60–80 K. We investigated a number of different samples, using contacts prepared by sputtered gold or silver paint and in all cases a behavior very similar to that of Fig. 2(a) was detected. While above about 150 K electrode polarization [11] prevents the detection of the intrinsic properties, the results with different contact types reveal that for lower temperatures any contact contributions are unlikely and the relaxational behavior can be regarded as intrinsic. However, we found a strong variation of the dc conductivity for different measurements, which seems to strongly depend on purity, defects, and thermal history of the samples. Concerning the origin of the polar moments, currently only speculations are possible, e.g., about an off-center position of the  $\text{Cr}^{3+}$  ions [3], similar to the situation in perovskite ferroelectrics (e.g.,  $\text{BaTiO}_3$ ), an intrinsic surface-related Maxwell-Wagner mechanism [4,12], or more exotic scenarios as, e.g., electronic ferroelectricity driven by charge order and/or coupling of the electron system to the lattice [13,14]. For  $\text{CdCr}_2\text{S}_4$ , the occurrence of ferroelectricity due to the softening of a polar mode has been excluded in recent LSDA +  $U$  calculations [15].

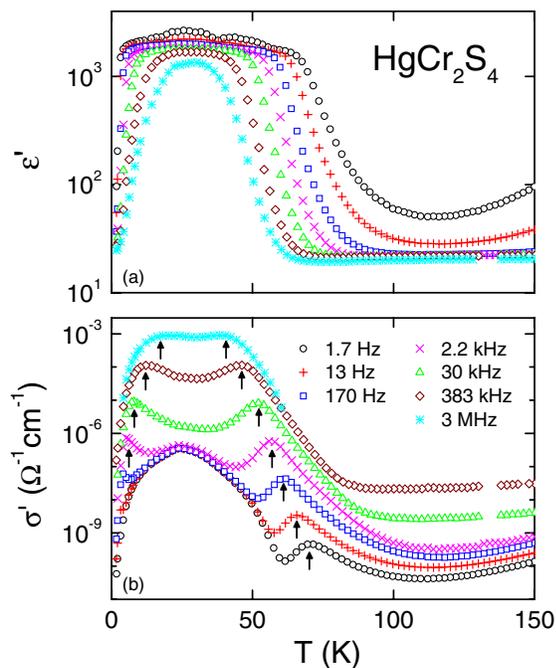


FIG. 2 (color online). Temperature dependence of dielectric constant (a) and conductivity (b) of  $\text{HgCr}_2\text{S}_4$  for various frequencies. The arrows in (b) indicate the positions of the relaxation peaks.

It is suggestive to assume a connection of the anomaly in  $\varepsilon'(T)$  at 60–80 K with the observation of FM correlations at 60 K [6–8]. Thus, as these correlations become strongly enhanced already in moderate external magnetic fields, in  $\text{HgCr}_2\text{S}_4$  a considerable magnetocapacitance may be expected. In Fig. 3(a), we show  $\varepsilon'$  measured at 30 kHz without and with a magnetic field of 5 T. The field indeed induces a strong shift of the upturn of  $\varepsilon'$  of about 50 K towards higher temperatures. This corresponds to a huge field-dependent increase of  $\varepsilon'$  in the region of 60–100 K. Similar behavior is also found at other measuring frequencies. As revealed by the inset of Fig. 3(a), the magnetocapacitance, defined as relative change of  $\varepsilon'$ , reaches a factor of up to 120. In Fig. 4,  $\varepsilon'(\nu)$  measured for different magnetic fields is shown revealing a steplike decrease with increasing frequency, again typical for a relaxational process. As the frequency of the point of inflection gives an estimate of the relaxation rate, its shifting to higher frequencies with increasing magnetic field gives evidence for an acceleration of the relaxational dynamics by the magnetic field. The inset of Fig. 4 demonstrates the strong increase of the dielectric constant in external magnetic fields, which critically depends on the measuring frequency. It is remarkable that, in contrast to the findings in  $\text{CdCr}_2\text{S}_4$  [3],  $\varepsilon'(T)$  at 5 T [Fig. 3(a)] does not show a final reduction at low temperatures due to the slowing down of relaxational dynamics. Instead, down to the lowest

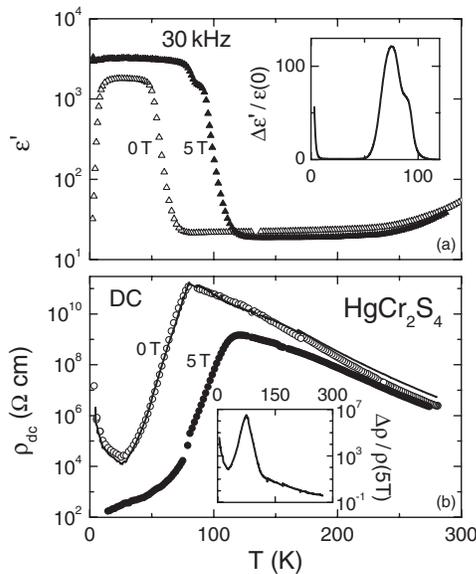


FIG. 3. (a) Temperature dependence of  $\varepsilon'$  at 30 kHz measured at zero field and in an external magnetic field of 5 T. The inset provides a measure of the magnetocapacitive effect, with  $\Delta\varepsilon' = \varepsilon'(5 \text{ T}) - \varepsilon'(0 \text{ T})$ . (b) Temperature dependence of the dc resistivity at zero field and in a magnetic field of 5 T measured in two-point contact configuration (symbols). In addition, the results of a four-point measurement at zero field is shown (line), scaled by a multiplicative factor to match the two-point result. The inset shows the relative change of the resistivity with  $\Delta\rho = \rho(0 \text{ T}) - \rho(5 \text{ T})$ .

temperature investigated (2.5 K),  $\varepsilon'(T)$  remains constant. One may speculate about tunneling processes playing a role here and further experiments at lower temperatures are necessary to clarify this issue.

In Fig. 3(b), the dc resistivity  $\rho_{\text{dc}}$  of  $\text{HgCr}_2\text{S}_4$ , measured using two-point (open circles) and four-point contact geometry (line) is shown. Because of the small sample dimensions it was not possible to prepare contacts of well-defined geometry for the four-point measurement. Thus, the resulting curve was scaled by a multiplicative factor to match the two-point curve leading to a good agreement. Since a contact resistance only could give rise to an *additive* contribution, which in addition should be temperature dependent, the good match of both curves gives further evidence that contact contributions can be neglected.  $\rho_{\text{dc}}(T)$  exhibits a strong anomaly at about 80 K, switching from semiconducting to metal-like temperature characteristics. Finally the semiconducting behavior is restored below 25 K when the system orders antiferromagnetically [6]. In an external magnetic field of 5 T, the anomaly is shifted to about 120 K, and the metal-like behavior is retained down to the lowest temperatures. This corresponds to a strong variation of  $\rho_{\text{dc}}$  with magnetic field. As shown in the inset of Fig. 3(b), its relative variation exceeds  $10^6$ , a truly colossal effect exceeding the findings in most CMR manganites [1]. Obviously the CMC in  $\text{HgCr}_2\text{S}_4$  is accompanied by the occurrence of CMR. It is unclear up to now what causes the anomaly at 80 K. Its strong shift to higher temperatures with magnetic field suggests a connection to the FM correlations reported in [6], but it seems extraordinary that a complete metal-insulator transition should occur as a result of magnetic fluctuations only. The magnetic-field-induced generation of a fully ordered FM state already below about 120 K leads to the detected CMR. Double exchange as in the CMR manganites [1] can be excluded in the present case,  $\text{Cr}^{3+}$  having a half-filled  $t_{2g}$  level. The observed CMR probably results from the reduction of spin-disorder scat-

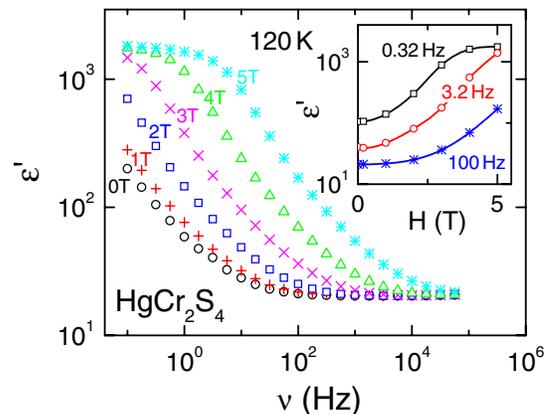


FIG. 4 (color online).  $\varepsilon'(\nu)$  at 120 K for various external magnetic fields between 0 and 5 T. The inset shows the field dependence for three selected frequencies.

tering in the FM state, an effect that may be strongly enhanced for low charge carrier densities [16].

We want to emphasize that the dc conductivity and the dielectric constant are independent quantities and an anomaly of one not necessarily leads to an anomaly of the other. While  $\epsilon'$  is related to  $\sigma'$  via the Kramers-Kronig relation, only ac conductivity, e.g., arising from hopping of localized charge carriers [17], but not dc conductivity, can induce a contribution in  $\epsilon'$ . ac conductivity, usually following a fractional power law  $\sigma' \propto \nu^s$  with  $s < 1$ , leads to a divergence of  $\epsilon'$  for decreasing frequency [17,18]. Thus the saturation at a value of about 2000, observed for low frequencies and high fields in Fig. 4, clearly excludes ac conductivity as an explanation of the observed CMC. However, from a theoretical point of view, e.g., based on the Clausius-Mosotti equation or other theoretical considerations [19,20], a simultaneous decrease of  $\rho_{dc}$  and increase of  $\epsilon'$  can arise when approaching a metal-insulator transition from the insulating side. Indeed such a behavior was observed in some doped semiconductors [19,21]. However, these predictions concern purely electronic contributions to the dielectric constant, which should not show any notable frequency dispersion in the frequency range of the present work. Nevertheless, it cannot be excluded that the electron system contributes via a coupling to atomic displacements as discussed, e.g., in [13]. Finally it should be noted that a coupling of  $\epsilon'$  and  $\rho_{dc}$  also can arise when assuming a Maxwell-Wagner relaxation process due to interfacial polarization [11]. Within this scenario, CMR can lead to a strong magnetocapacitance [22]. Maxwell-Wagner relaxations can occur due to electrode polarization [11], which seems unlikely based on our results with varying contact preparation. However, we cannot fully exclude an internal boundary mechanism as discussed, e.g., in [12] for  $\text{CdCr}_2\text{S}_4$ , a possibility that needs to be further investigated.

In summary, the spinel compound  $\text{HgCr}_2\text{S}_4$  shows the simultaneous occurrence of CMC and CMR, both of exceptionally large magnitude. Especially, despite this material exhibits no long-range FM order, its magnetocapacitance exceeds by far that observed in the FM spinel compounds  $\text{CdCr}_2\text{S}_4$  [3,4] and  $\text{CdCr}_2\text{Se}_4$  [5]. The reason for the exceptional behavior of  $\text{HgCr}_2\text{S}_4$  must be found in the strong magnetic frustration as revealed by magnetic and specific-heat studies [6]. It was suggested to lead to a complex AFM ground state, which can be easily switched into a FM state by moderate fields. Interestingly, structural investigations indicate that the system is close to a structural instability and that there is a possible off-center displacement of the  $\text{Cr}^{3+}$  ions [6]. It was speculated already in [3] that such an off-center position, in conjunction with geometrical frustration, could lead to a relaxor FE state and that the coupling of the relaxational dynamics to the magnetic order parameter may arise from a softening of the lattice via exchangestriction. A relaxor state, with its

nanoscale FE ordering, would explain the absence of a true long-range structural transition. But also other scenarios seem possible and further work has to be done to clarify the origin of the amazing magnetoelectrical properties of the chalcogenide-chromium spinels.

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- [1] K. Chahara *et al.*, Appl. Phys. Lett. **63**, 1990 (1993); R. von Helmolt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin *et al.*, Science **264**, 413 (1994); A. P. Ramirez, J. Phys. Condens. Matter **9**, 8171 (1997); E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
- [2] T. Kimura *et al.*, Nature (London) **426**, 55 (2003); N. Hur *et al.*, *ibid.* **429**, 392 (2004); Th. Lottermoser *et al.*, *ibid.* **430**, 541 (2004); T. Goto *et al.*, Phys. Rev. Lett. **92**, 257201 (2004); N. Hur *et al.*, *ibid.* **93**, 107207 (2004).
- [3] J. Hemberger *et al.*, Nature (London) **434**, 364 (2005).
- [4] P. Lunkenheimer *et al.*, Phys. Rev. B **72**, 060103(R) (2005).
- [5] J. Hemberger *et al.*, cond-mat/0508014.
- [6] V. Tsurkan *et al.*, cond-mat/0603348.
- [7] J. M. Hastings and L. M. Corliss, J. Phys. Chem. Solids **29**, 9 (1968).
- [8] H. W. Lehmann and G. Harbeke, Phys. Rev. B **1**, 319 (1970).
- [9] L. Pintilie and M. Alexe, Appl. Phys. Lett. **87**, 112903 (2005).
- [10] A. E. Glazounov and A. K. Tagantsev, J. Phys. Condens. Matter **10**, 8863 (1998).
- [11] P. Lunkenheimer *et al.*, Phys. Rev. B **66**, 052105 (2002); **70**, 172102 (2004).
- [12] M. Toda, *Proceedings of the 3rd Conference on Solid State Devices, Tokyo, 1971* (Japanese Society of Applied Physics, Tokyo, 1972), supplement to Oyo Buturi, Vol. 41, p. 183.
- [13] P. Monceau *et al.*, Phys. Rev. Lett. **86**, 4080 (2001); D. Starešinić *et al.*, *ibid.* **96**, 046402 (2006).
- [14] N. Ikeda *et al.*, Nature (London) **436**, 1136 (2005).
- [15] C. J. Fennie and K. M. Rabe, Phys. Rev. B **72**, 214123 (2005).
- [16] P. Majumdar and P. B. Littlewood, Nature (London) **395**, 479 (1998).
- [17] A. R. Long, Adv. Phys. **31**, 553 (1982); S. R. Elliott, *ibid.* **36**, 135 (1987).
- [18] A. K. Jonscher, *Dielectric Relaxations in Solids* (Chelsea Dielectrics Press, London, 1983).
- [19] T. G. Castner, Philos. Mag. B **42**, 873 (1980).
- [20] C. Aebischer, D. Baeriswyl, and R. M. Noack, Phys. Rev. Lett. **86**, 468 (2001).
- [21] H. F. Hess *et al.*, Phys. Rev. B **25**, 5578 (1982).
- [22] G. Catalan, Appl. Phys. Lett. **88**, 102902 (2006).