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Multiferroic behavior in CdCr_2X_4 ($\text{X} = \text{S}, \text{Se}$)

J. Hemberger^{a,b,*}, P. Lunkenheimer^b, R. Fichtl^b, S. Weber^b, V. Tsurkan^{b,c}, A. Loidl^b

^a*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany*

^b*Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, D-86135 Augsburg, Germany*

^c*Institute of Applied Physics, Academy of Sciences of Moldova, str. Academiei 5, MD 2028, Chisinau, Republic of Moldova*

Multiferroic materials at least two (in a strict sense) order parameters corresponding to different degrees of freedom coexist simultaneously. This scenario can combine, e.g., ferro-orbital order, ferroelectricity, ferromagnetism, or ferroelectricity. Especially the coexistence of the latter properties, namely ferroelectricity and ferromagnetism, is rarely found and has been a “hot” topic in recent solid state research [1–3]. The simultaneous coupling of both sectors, i.e. the strong coupling of electric (magnetic) properties under application of an electric (magnetic) field, which is found in some materials, makes them highly attractive not only from a fundamental point of view, but also for potential applications in microelectronics. In the present contribution we report on magnetization, dielectric polarization, as well as broadband dielectric measurements in the multiferroic systems CdCr_2S_4 and CdCr_2Se_4 and provide detailed information on the dielectric relaxation dynamics in the paramagnetic and ferromagnetic state. For these

investigations special emphasis was put on the influence of contacts on the dielectric characterization comparing sputtered gold- and silver-paint electrodes applied on opposite sides of the plate-like single crystalline samples. Dielectric constant and loss were measured over a broad frequency range ($3 \text{ Hz} < \nu < 3 \text{ GHz}$) using frequency-response analysis and a reflectometric technique [4]. Electric polarization was detected employing a high-impedance Sawyer–Tower circuit and the magnetization data were recorded with a commercial SQUID magnetometer (MPMS, QuantumDesign).

At room temperature, the recently discovered multiferroic CdCr_2S_4 is a cubic spinel compound [3]. The Cd^{2+} ions on the structural A-sites carry neither a magnetic nor an orbital degree of freedom. The Cr^{3+} ions on the octahedrally surrounded B-sites possess half-filled t_{2g} shells and thus also are orbitally inactive but due to Hund’s coupling and a quenched orbital moment carry a $S = J = \frac{3}{2}$ spin configuration. It shall be noted, that the absence of a Jahn–Teller active orbital degree of freedom and the high crystallographic symmetry allow for a relaxation of the structure into polar distortions. The spins are coupled ferromagnetically and as can be seen in the upper frame of Fig. 1 magnetic order sets in at $T_c \approx 84 \text{ K}$. At the same time a steep increase of the dielectric constant can be

*Corresponding author. Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, D-86135 Augsburg, Germany. Tel.: +49 821 598 3616; fax: +49 821 598 3649.

E-mail address: joachim.hemberger@physik.uni-augsburg.de (J. Hemberger).

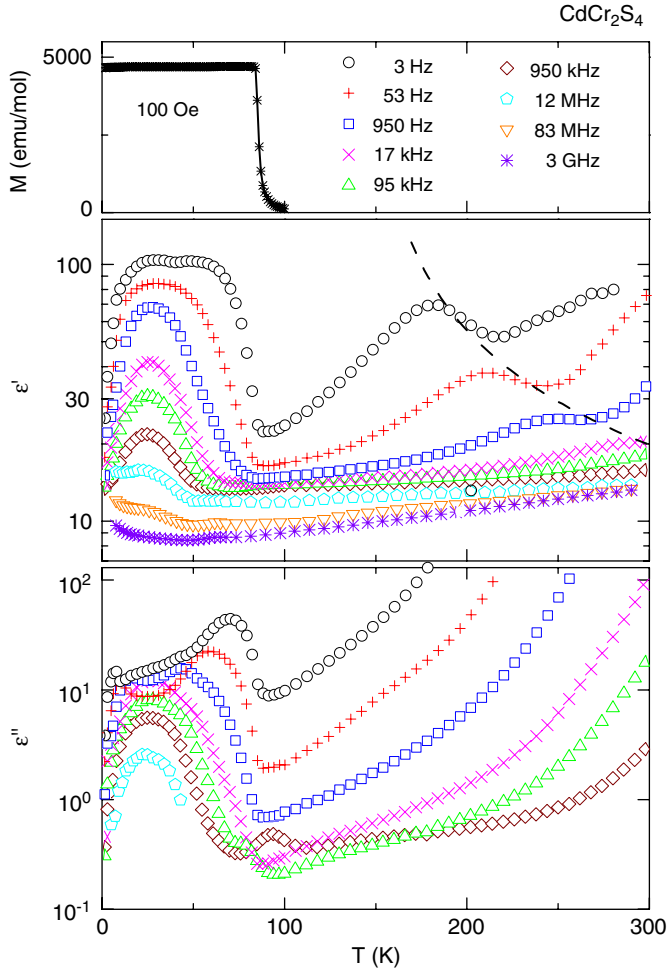


Fig. 1. Temperature dependence of the low field magnetization (upper frame) and complex dielectric permittivity ϵ^* (lower frames) of CdCr_2S_4 for various frequencies. The magnetic transition occurs at $T \approx 84$ K and is accompanied by an increase of the permittivity towards low temperatures. (Note, that the plateau-like low-temperature value of the magnetization is determined by the demagnetization factor of the sample in the small measurement field of $H = 100$ Oe and does not display an intrinsic saturation.)

detected, which for low frequencies reaches relatively high values above $\epsilon' \approx 100$ (Fig. 1, middle frame). The details of the frequency dependence of the complex permittivity will be discussed below, but before it shall be pointed out that the low-temperature phase of CdCr_2S_4 exhibits not only spontaneous magnetization but in addition the high values of ϵ' can be interpreted as precursor of the onset of remnant dielectric polarization at lower temperatures. Fig. 2 shows hysteresis loops taken at $T = 25$ K for both the magnetic as well as the dielectric sector. $M(H)$ shows the characteristics of a soft ferromagnet reaching nearly the full magnetic moment of $6\mu_B$ expected for two Cr^{3+} ions per formula unit. The small deviations from the full value can be attributed to pronounced magnon features typical for such systems. At the same time the $P(E)$ curve is quite slim and smeared out. No real saturation value is reached within the experimentally accessible electric field range of 400 kV/m and no well-defined coercive electric field strength can be

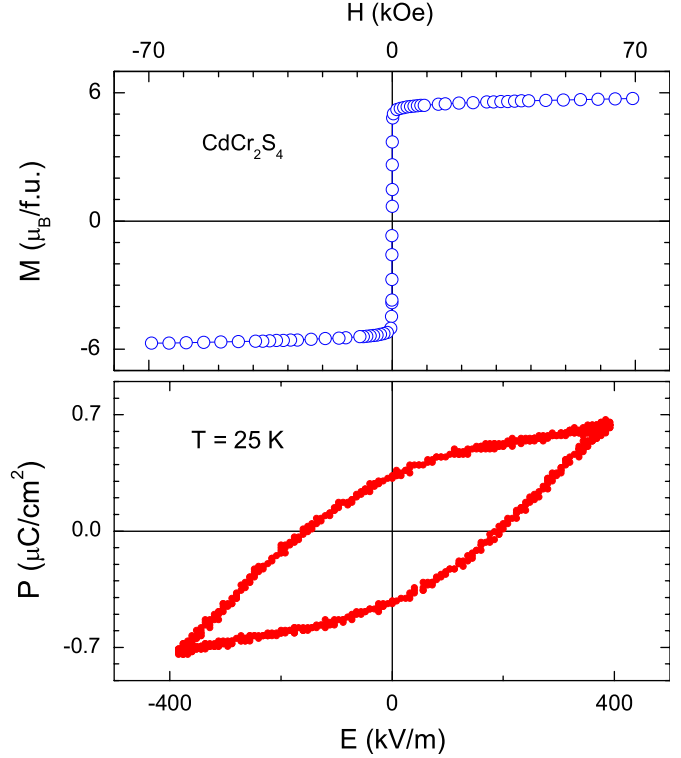


Fig. 2. Hysteresis loops for the magnetic ($M(H)$, upper frame) and dielectric sector ($P(E)$, lower frame) measured at $T = 25$ K. The magnetic data were mirrored and corrected for demagnetization effects; the polarization data were measured at $\nu = 1.13$ Hz.

identified. Such type of hysteresis behavior is typical for so-called relaxor-ferroelectric behavior, where nano-scale ferroelectric clusters determine the polarization response [5].

Such type of behavior is also evidenced by the frequency and temperature dependence of the complex permittivity in CdCr_2S_4 . Fig. 1 shows real and imaginary part of the dielectric constant, $\epsilon'(T)$ and $\epsilon''(T)$, for frequencies from 3 Hz to 3 GHz. For $T > 100$ K, in $\epsilon'(T)$ a peak shifting to lower temperatures and increasing in amplitude with decreasing frequency shows up. The dashed line indicates a Curie-Weiss law, $\propto 1/(T - 135 \text{ K})$, for the right flank of the peaks, which can be taken as an estimate of the static dielectric constant. The further increase of $\epsilon'(T)$ towards higher temperatures is due to contact and conductivity contributions as discussed below. Thus, the overall characteristics of the relaxational behavior in CdCr_2S_4 resemble that observed in relaxor ferroelectrics [5]. There the reduction of ϵ' below the peak temperature is usually ascribed to a cooperative freezing-in of ferroelectric clusters on the time scale given by the frequency of the applied AC electric-field, quite in contrast to canonical ferroelectrics where the frequency dependence of $\epsilon'(T)$ is negligible. Such relaxational features seen in the real part of the permittivity should be accompanied by peaks in the imaginary part. At $T > T_c$ in CdCr_2S_4 , they should appear at the frequency of the point of inflection at the left wing of the maxima in $\epsilon'(T)$. However, no such peaks become obvious in Fig. 1, which can be ascribed to superimposing

contributions from charge carrier transport. As the dielectric loss and the real part of the conductivity are linked via the relation $\varepsilon'' \propto \sigma'/\nu$, the staggered behavior of the dielectric loss curves can be attributed to the presence of conductivity contributions.

The most remarkable feature in Fig. 1 is the strong increase of $\varepsilon'(T)$ below the ferromagnetic transition temperature $T_c = 84$ K, indicating the close coupling of magnetic and dielectric properties. It can be explained assuming that the frozen-in dynamics of the dielectric relaxor entities are melting due to the onset of magnetization and become fast again, which restores a large contribution in the dielectric response [6]. At the same time the dielectric loss is increasing below T_c . As mentioned before, this in part may be influenced by changes in the conductivity. Magnetoresistive effects have been reported for CdCr_2S_4 and CdCr_2Se_4 in the literature [7].

For CdCr_2Se_4 , the magnetic transition is shifted to higher temperatures. The magnetic order sets in at $T_c \approx 125$ K as monitored in the upper frame of Fig. 3. At this temperature an increase of $\varepsilon'(T)$ towards lower temperatures is detected, too. Thus, similar to CdCr_2S_4 [3], the closely related CdCr_2Se_4 also exhibits a strong magneto-dielectric coupling. The typical relaxor peaks in the real part of the permittivity at $T > T_c$ are shifted to higher temperatures and only can be detected for the lowest frequencies within the examined temperature regime below 300 K. The superimposed influence of conductivity is higher in CdCr_2Se_4 compared to CdCr_2S_4 . For this in the lowest frame of Fig. 3, σ' is plotted. For low frequencies the data fall onto one curve reflecting the DC value of conductivity. The higher-frequency curves successively branch off from this curve pointing to additional relaxational and/or AC conductivity contributions.

It has to be mentioned that even though the observed effects are stable against the exchange of the chalcogen ion, the occurrence of the observed dielectric features depends sensitively on the stoichiometry. Annealing of the samples, both, in vacuum or sulfur/selen atmosphere, leads to a suppression of the frequency depend relaxor peaks in $\varepsilon'(T)$ above T_c and no remanent electric polarization can be found at low temperatures. Also, these features so far could not be detected in polycrystalline samples.

Also, one should consider the possibility that the observed relaxation features are not a bulk property, but of the so-called Maxwell–Wagner type [8], i.e. caused by polarization effects at or close to the surface of the samples. A prominent example for Maxwell–Wagner relaxations are the so-called “colossal dielectric constant” materials [9]. In most (if not all) of these materials, relaxational behavior with very high (typically 10^3 – 10^5), non-intrinsic dielectric constants arise from the formation of depletion layers at the interface between sample and metallic contacts. The high capacitance of these insulating layers at the sample surface can lead to apparently high dielectric constants and relaxational behavior. Thus in the present case, we varied the electrode materials, to check for such a scenario. Fig. 4

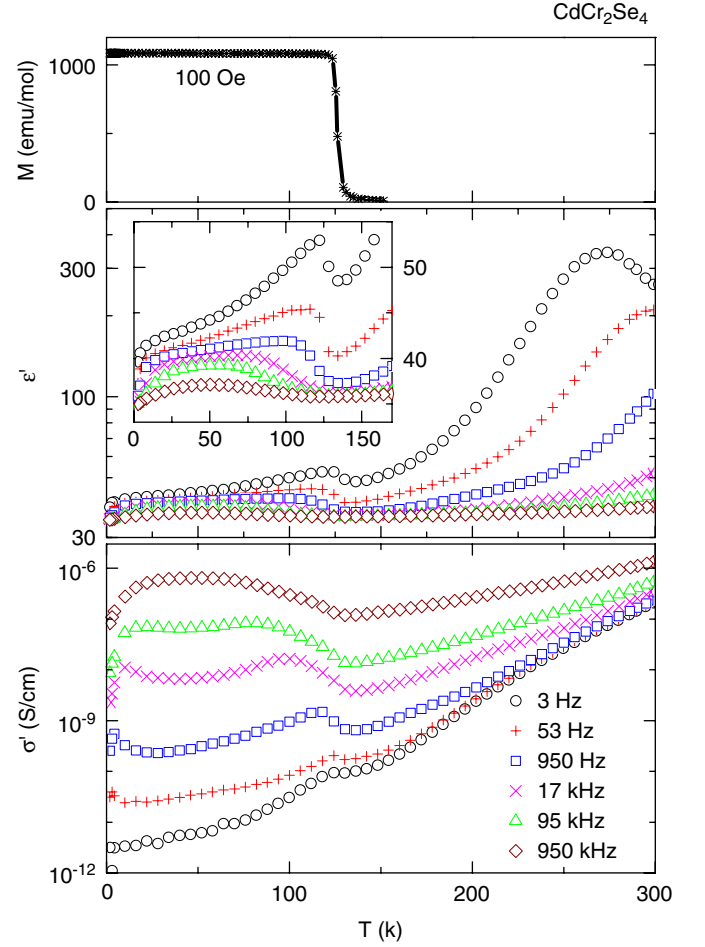


Fig. 3. Temperature dependence of the low field magnetization (upper frame), real part of the dielectric permittivity ε' (middle), and real part of the conductivity (lower frame) of CdCr_2Se_4 for various frequencies. The magnetic transition occurs at $T \approx 125$ K and is accompanied by an increase of the permittivity towards low temperatures. (Note, that the plateau-like low-temperature value of the magnetization is determined by the demagnetization factor of the sample in the small measurement field of $H = 100$ Oe and does not display an intrinsic saturation.)

shows measurements of $\varepsilon'(T)$ for contacts made from silver-paint or sputtered gold. For high temperatures significant differences between both measurements can be detected. However, the relaxation features are still present at the same temperatures and for temperatures below the data match each other. This clearly points towards a dominance of intrinsic effects.

Concerning the microscopic origin of the polar moments in CdCr_2S_4 and CdCr_2Se_4 it can be assumed that the ferroelectric distortions result from an off-center position of the Cr^{3+} -ions which generates a locally polar but macroscopically isotropic cluster state [10]. Geometrical frustration within the at room temperature highly symmetric cubic lattice drives the observed relaxor-like freezing [11]. On the other hand, the origin of the strong coupling of magnetization and dielectric permittivity in this compound is so far unknown. As pointed out the relaxation dynamics of the polar moments are accelerated below T_c [6], but it

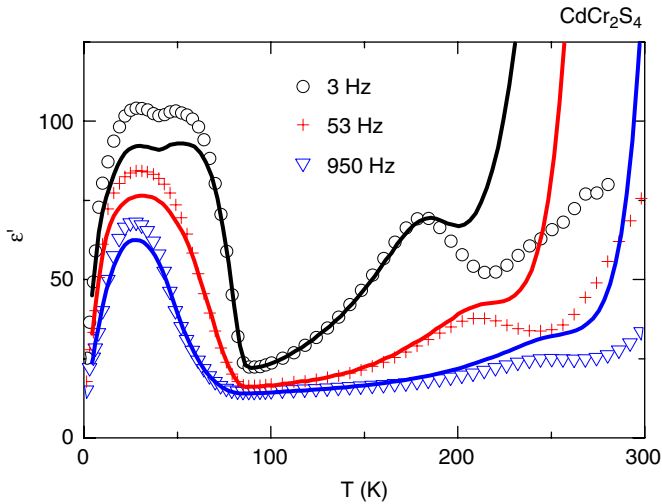


Fig. 4. Temperature dependence of the real part of the dielectric permittivity ϵ' of CdCr_2S_4 measured for various frequencies. The symbols represent measurements employing sputtered gold electrodes; the lines denote the results obtained with electrodes of silver paint.

remains to be clarified what is the microscopic origin of the detected relaxation dynamics and why this dynamics couples so strongly to the magnetic order parameter. A coupling via exchangestriction, i.e. volume changes arising from the magnetic exchange energy [12] seems possible. The onset of spin order leads to a softening of the lattice thereby reducing the energy barriers against dipolar reorientation and thus enhancing the mean relaxation rate. As an alternative explanation one could consider a magnetic-field-induced variation of charge-carrier mobility or density. As mentioned before, a sizable DC magnetoresistive effect is well known for CdCr_2S_4 [7], but it cannot be responsible for the observed anomalies of ϵ' as the DC resistivity only contributes to ϵ'' . In contrast, hopping-type charge transport is known to give rise to frequency-dependent AC conductivity, which via the Kramers–Kronig relation would lead to a contribution to the dielectric constant [13].

In conclusion, our results clearly reveal that in CdCr_2S_4 and CdCr_2Se_4 canonical ferromagnetism coexists at sizable ordering temperatures with a relaxor-ferroelectric state,

characterized by a significant relaxational behavior. Both order parameters are strongly coupled. There is a radical change of the dielectric relaxational dynamics driven by the onset of magnetization that leads to the observed strong increase of the dielectric permittivity in these compounds. The present dielectric experiments cannot provide final evidence on the microscopic origin of this puzzling behavior. While contact effects could be ruled out and the influence of charge transport seems unlikely, a scenario in which the relaxation mechanism interacts with magnetic order via exchangestriction can be considered the most plausible.

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