

Theoretical Study of the Multiferroic Behavior of the Magnetic Relaxor Ferroelectric CdCr₂S₄

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Abstract

Using a microscopic model and the replica method as well as the Green's function theory, we have investigated the relaxor and multiferroic behavior of CdCr₂S₄. The magnetization, the remanent polarization P_r and the real part of the dielectric function ϵ' are studied theoretically as a function of temperature, with and without a magnetic field, respectively. The magnetization and the polarization exist together below the magnetic phase transition temperature. P_r decreases whereas ϵ' increases and the peak shifts to smaller temperature values with increasing magnetic field h . Moreover, the temperature and electric field E dependence of the magnetization M is also discussed. A kink is observed around the ferroelectric transition temperature. The kink is deeper for stronger electric fields and anharmonic spin-phonon interactions.

Keywords

Multiferroic CdCr₂S₄, Microscopic Model, Polarization, Dielectric Function

1. Introduction

The magnetic relaxor ferroelectric materials with the coexistence of relaxor ferroelectricity and magnetic order have been attracting considerable attention due to their peculiar properties and various applications [1] [2] [3] [4]. Basic components of this family of materials are the chromium chalcogenide and the compounds that have the general formula ACr₂X₄, where A = Cd or Hg, X = S or Se. These crystals are generally found in the cubic spinel structure. It is well known that Cr³⁺ with spin $S = 3/2$ is responsible for the magnetic properties [5]. As a relaxor ferroelectric, structural investigation indicates that the system is close to a structural instability and there is a possible off-center displacement of

Cr^{3+} ions [6] [7]. Such an off-center position, in conjunction with geometrical frustration, leads to a relaxor ferroelectric state [2]. A spin-glass-like behavior in ferromagnetic phase of CCS is reported by Kitani *et al.* [8]. The occurrence of a multiferroic state in various spinel systems, including CCS [2] [3] [9] [10], FeCr_2S_4 (FCS) [11], CdCr_2Se_4 (CCSe) [10] and HgCr_2S_4 (HCS) [4] is reported. In CdCr_2S_4 (CCS) the ferromagnetic and ferroelectric transitions were found at 84 and 57 K, respectively. An evident anomaly in the dielectric constant at $T_C = 84$ K has been reported [2] [3], indicating the magnetoelectric coupling between magnetism and dielectric properties. Magnetic and electric field dependent dielectric and magnetic properties are studied in multiferroic CCS by Sun *et al.* [12]. Concerning the microscopic origin of the polar moments in CCS and CCSe 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 [13]. The results of Grimes *et al.* [13] revealed that in CCS and CCSe canonical ferromagnetism coexists at sizable ordering temperatures with a relaxor-ferroelectric state, characterized by a significant relaxational behavior. Both order parameters are strongly coupled. A scenario in which the relaxation mechanism interacts with magnetic order via exchange striction can be considered the most plausible.

There are not so many theoretical investigations of the properties of magnetic relaxor ferroelectrics. Fennie and Rabe [14] have studied the dielectric properties of the ferromagnetic spinel CCS from first principles. The observed results suggested that the observed anomalous dielectric behavior in CCS is not due to the softening of a polar mode. Oliveira *et al.* [7] have used the Landau theory to demonstrate that a linear coupling between the magnetic and polar order parameters (*aPM*) is sufficient to justify the appearance of magnetic cluster in the paramagnetic phase of CCS. Zhou *et al.* [15], based on the spherical random-bond-random-field model and the Heisenberg model, considering the coupling interaction between the relaxor ferroelectricity and magnetism, have calculated the third-order static nonlinear dielectric susceptibility as well as the scaled nonlinear susceptibility of magnetic relaxor ferroelectrics. The important role of the fluctuations of the spin-pair correlations in the change of the dielectric susceptibility around the magnetic phase transition temperature is shown by Xia and Jiang [16] [17] based on the spherical random-bond-random-field (SRBRF) model, the Heisenberg model and a magnetoelectric coupling term. Using the same model Cao *et al.* [18] have investigated the influence of Fe substitution on the magnetic and static nonlinear dielectric response in the doped magnetic relaxor ferroelectrics CCS. Band structure calculations for ACr_2X_4 ($A = \text{Zn}, \text{Cd}, \text{Hg}$ and $X = \text{O}, \text{S}, \text{Se}$) spinels are presented by Yaresko [19].

The aim of the present paper is to study the effect of an applied static magnetic field on the dielectric properties of magnetic relaxor ferroelectric CCS using a microscopic model and the replica method as well as the Green's function theory.

2. The Model

Pioneering studies of magnetic semiconductors in the 1960s showed the coexistence of semiconduction and magnetism in some ferromagnetic semiconductors, such as europium chalcogenides and the spinel compounds CCS and CCSe [20]. But in the last years they are considered as materials as magnetic relaxor ferroelectrics. The Hamiltonian which can describe their magnetic and relaxor ferroelectric properties is:

$$H = H_m + H_f + H_{mf}. \quad (1)$$

H_m is the s-d Hamiltonian:

$$H_m = H_s + H_e + H_I. \quad (2)$$

H_s is the Heisenberg Hamiltonian for the ferromagnetically ordered d electrons,

$$H_s = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i \mathbf{h} \cdot \mathbf{S}_i + H_{sp}, \quad (3)$$

where \mathbf{S}_i is the Heisenberg operator of Cr^{3+} at the lattice site i . Ferromagnetic order in CCSe and in CCS appears below $T_{Cm} = 130$ K and 84 K, respectively, as a result of competition between the direct Cr-Cr spin coupling and the near neighbour Cr-Se(or S)-Cr exchange interactions. The exchange interaction J_{ij} is a function of the lattice constant and stands for the nearest neighbors $J_1 > 0$ and next nearest neighbors $J_2 < 0$. The frustration plays an important role in these materials. \mathbf{h} is an applied magnetic field.

Strong spin-phonon interaction is reported in CCS [12] [21] [22] [23]:

$$H^{sp} = -\frac{1}{2} \sum_{i,j} F(i,j) Q_i S_j^z - \frac{1}{4} \sum_{i,j,r} R(i,j,r) Q_i Q_j S_r^z + h.c. \quad (4)$$

Q_i is the normal coordinate of the lattice mode. F and R designate the amplitudes for coupling of phonons to the spin excitations in first and second order, respectively. h.c. represents the hermitian conjugate.

H_e is the usual Hamiltonian of the conduction band electrons,

$$H_e = \sum_{\mathbf{q},\sigma} (\epsilon_{\mathbf{q},\sigma} - \mu) a_{\mathbf{q}\sigma}^+ a_{\mathbf{q}\sigma}, \quad (5)$$

where a^+ and a are the Fermi creation and annihilation operators, μ is the chemical potential, and $\epsilon_{\mathbf{q},\sigma}$ are the Bloch energies.

H_I couples the two subsystems (3) and (4) by an intraatomic exchange interaction I

$$H_I = -\frac{I}{2N} \sum_{\mathbf{q},\mathbf{p}} \left[S_{\mathbf{q}-\mathbf{p}}^+ a_{\mathbf{p}-}^+ a_{\mathbf{q}+} + S_{\mathbf{q}-\mathbf{p}}^- a_{\mathbf{p}+}^+ a_{\mathbf{q}-} + S_{\mathbf{q}-\mathbf{p}}^z (a_{\mathbf{p}+}^+ a_{\mathbf{q}+} - a_{\mathbf{p}-}^+ a_{\mathbf{q}-}) \right]. \quad (6)$$

The Hamiltonian of the relaxor ferroelectric subsystem H_f in the presence of an electric field can be written as [24]

$$H_f = -\frac{1}{2} \sum_{(k,l)} A_{kl} \bar{\sigma}_k \cdot \bar{\sigma}_l - \sum_k \tilde{\mathbf{h}}_k \cdot \bar{\sigma}_k - \sum_k \mathbf{E} \cdot \bar{\sigma}_k. \quad (7)$$

(k, l) means the summation over each distinct pair once, and σ_k is a dimensionless order parameter field. A_{kl} and $\tilde{\mathbf{h}}_k$ are randomly frustrated bonds and random fields, respectively, which are satisfied with a Gaussian distribution. The last are characterized by the variance Δ . A_{kl} is specified by its random average value A_0 and root-mean-square variance A^2 . \mathbf{E} is an applied electric field. A ferroelectric ordering in CCS occurs near $T_{Cf} = 56$ K.

There are four order parameters—the localized-spin magnetization M for arbitrary spin S , the conduction-electron magnetization ρ , the polarization P and the spin glass order parameter q which are given by:

$$M = \langle S^z \rangle = \frac{1}{N^2} \sum_{i,j} \left[(S + 0.5) \coth \left[(S + 0.5) \beta E_{ij} \right] - 0.5 \coth \left(0.5 \beta E_{ij} \right) \right], \quad (8)$$

$$\rho = \frac{1}{2N} \sum_{\mathbf{q}, \sigma} \sigma \langle a_{\mathbf{q}\sigma}^+ a_{\mathbf{q}\sigma} \rangle, \quad \sigma = \pm 1 \quad (9)$$

$$P = \beta (1 - q) (A_{0eff} P + E), \quad (10)$$

$$q = \beta^2 A_{eff}^2 \left(q + \Delta / A_{eff}^2 \right) (1 - q)^2 + P^2, \quad (11)$$

with the renormalized exchange interaction constants:

$$A_{0eff} = A_0 - 2g \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle, \quad (12)$$

$$A_{eff}^2 = A^2 - 4g \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle + 4g^2 \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle^2. \quad (13)$$

The magnetoelectric coupling term between the magnetic (3) and electric (7) subsystems in the magnetic relaxor ferroelectric CCS and CCSe is proposed to be linear in the electric order parameter and quadratic in the magnetic order parameter:

$$H_{mf} = g \sum_{ijk} \bar{\sigma}_i \mathbf{S}_j \cdot \mathbf{S}_k, \quad (14)$$

where g is the magnetoelectric coupling constant. It must be noted that Xia and Jiang [16] [17] have chosen a biquadratic magnetoelectric coupling—quadratic in the electric and quadratic in the magnetic order parameters. But this coupling is suitable for multiferroics with very different phase transition temperatures, $T_{Cf} \gg T_{Cm}$, for example in BiFeO₃ or hexagonal RMnO₃. But this is here not the case, because both temperatures are close to another, $T_{Cf} \leq T_{Cm}$ [2], similarly to RMn₂O₅, which corresponds to a linear magnetoelectric coupling.

The correlation functions are calculated using the Green's functions $G_{ij} = \langle S_i^+; S_j^- \rangle$ and $g_{ij} = \langle a_i^+; a_j \rangle$. All quantities are renormalized due to the magnetoelectric and spin-phonon coupling and must be calculated selfconsistently.

3. Numerical Results and Discussion

The temperature dependence of the magnetization and polarization are numerically calculated taking parameters appropriated for CdCr₂S₄: $J_1 = 0.1$ eV, $J_2 = -0.05$ eV, $I = 0.3$ eV [25], $S = 3/2$, $F = 4$ cm⁻¹, $R = -0.35$ cm⁻¹, $T_{Cm} = 84$ K, $T_{Cf} =$

56 K, $A = 0.1$ eV, $g = 0.3$ eV.

The spin-phonon interaction taken up to second order and the magnetoelectric coupling g renormalize the exchange interaction constant J_1 to J_1^{eff} which is now temperature dependent:

$$J_1^{eff} = J_1 + \frac{2F^2}{\omega_0 - MR} + 2g \langle \tilde{\sigma} \rangle, \quad (15)$$

where M is the magnetization and ω_0 is the unrenormalized phonon energy.

By the calculation of the remanent polarization $P_r(T)$ we have included an electric field of $E = 100$ kV/m because there is no ferroelectric transition except in applied electric fields what is typical for relaxor ferroelectrics [26]. The results of M and P_r are presented in **Figure 1** and **Figure 2**, respectively. They show a coexistence of ferromagnetism and relaxor ferroelectricity together below nearly $T = 56$ K, *i.e.* below the ferroelectric phase transition temperature T_{Cf} . There is a

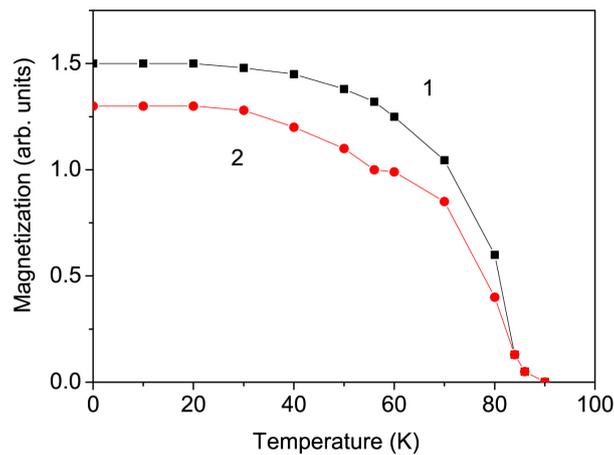


Figure 1. Temperature dependence of the magnetization M in CCS for 500 Oe and different electric field values: $E = 0$ (1), 100 kV/m (2).

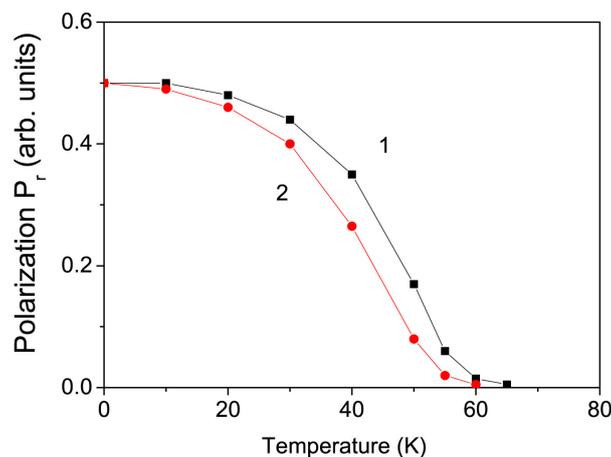


Figure 2. (Color online) Temperature dependence of the remanent polarization P_r in CCS for $E = 100$ kV/m and different magnetic field values: $h = 0$ (1), 500 Oe (2).

diffuse ferroelectric phase transition, which is characteristic for relaxor ferroelectrics. We have studied also the magnetic field dependence of the remanent polarization. P_r and T_{Cf} decrease with increasing magnetic field h (Figure 2, curve 2) what is evidence for a multiferroic behavior. The observed results are in good qualitative agreement with the experimental data of Hemberger *et al.* [2].

A strong decrease in the magnetization M is observed well below $T_{Cm} = 85$ K with increasing the external electric field E (Figure 1, curve 2). There is a kink around the ferroelectric phase transition T_{Cf} . The kink increases with increasing E in agreement with the experimental data of Sun *et al.* [12]. This anomaly is due to the magnetoelectric coupling g . It is evidence for the strong correlation among magnetic spin, electric dipole and the lattice in the multiferroic CCS. It must be noted that with increasing spin-phonon interaction R the kink in the temperature dependence of M is deeper and clearer. This shows the importance of the anharmonic spin-phonon interaction and that it must be taken into account in order to obtain correct results. We have observed a similar kink in the temperature dependence of the magnetization in the multiferroic RMn_2O_5 [27], where is also valid $T_{Cf} < T_{Cm}$.

We have calculated also the dielectric function ϵ from the expression [28]:

$$\left[\left(\frac{\Lambda}{\epsilon(\mathbf{k}, E) - 1} \right)_{\alpha\beta} + \Lambda \frac{k_\alpha k_\beta}{k^2} \right] \tilde{G}^{\beta\gamma}(\mathbf{k}, E) = \delta_{\alpha\gamma}; \quad \Lambda = 4\pi Z^2/v, \quad (16)$$

where Z is the electron charge and v is the volume, \tilde{G} is the ferroelectric Green's function.

The temperature and magnetic field dependence of the real part of ϵ is shown in Figure 3. The dielectric function ϵ' of CCS becomes strongly enhanced in the region below the ferromagnetic transition temperature $T_{Cm} = 84$ K which is strongly correlated with the ferromagnetic ordering. Exchange striction [2] [21], which mechanically induces the strain, is associated with the ferromagnetic

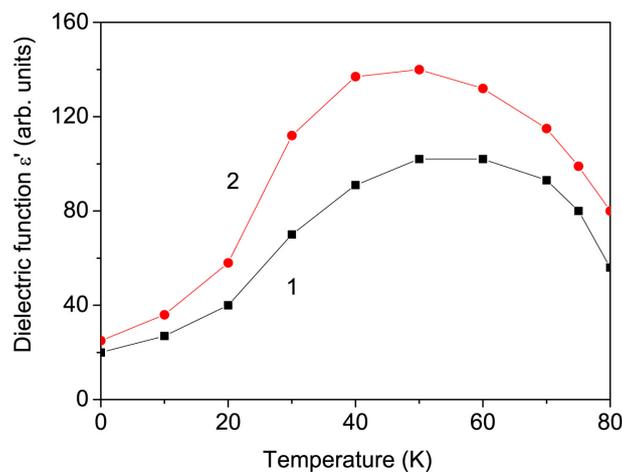


Figure 3. (Color online) Temperature dependence of the real part of the dielectric function ϵ' for $E = 100$ kV/m and different magnetic field values: $h = 0$ (1), 500 Oe (2).

ordering around T_{cm} and local lattice distortion takes place inducing the enhancement of dielectric constant. It goes through a broad maximum, which indicates a diffuse phase transition. This broad peak of $\epsilon'(T)$ is typical for a relaxor ferroelectric. The observed behavior is in accordance with the experimental data for CCS [2]. The low temperature peak is due to magnetic ordering, which shows that the magnetic and electric orders are coupled. All these characteristics are signatures of the relaxor state of magnetic relaxor ferroelectrics, in agreement with previous reports [4] [10].

The ferroelectric properties strongly depend on the external magnetic field h in multiferroics. Therefore, we have calculated also the magnetic field dependence of ϵ' in CCS, see **Figure 3**, curve 2. The dielectric function ϵ' increases with increasing h in agreement with the experimental data of Hemberger *et al.* [2] and Sun *et al.* [12]. The maximum is shifted to smaller temperature values. A similar shift of ϵ' is reported by Sun *et al.* [12]. It must be noted that Hemberger *et al.* [2] and Krohns *et al.* [9] also observed an increase of the dielectric function ϵ' with increasing the magnetic field and nonzero frequencies in CCS, but the peak shifts to higher temperature values. It must be noted that our calculations are for zero frequencies. In HCS Weber *et al.* [4] demonstrated also the strong increase of the dielectric constant in external magnetic fields.

4. Conclusions

The temperature and magnetic field dependence of relaxor characteristics such as remanent polarization P_r and real part of the dielectric function ϵ' are investigated theoretically for CCS. The relaxor polarization and the magnetization appear together below $T \sim 56$ K, *i.e.* below the ferroelectric phase transition temperature T_{cf} . A diffuse ferroelectric phase transition and a broad peak for ϵ' are observed which are typical for relaxor ferroelectrics, such as CCS. The polarization decreases whereas the dielectric function increases and the maximum of ϵ' shifts to higher temperature values with increasing the magnetic field h . It is shown that CCS is a multiferroic and that the relaxor behavior of magnetic relaxor ferroelectrics such as CCS can be controlled by the application of an external magnetic field.

The magnetization M decreases with increasing electric field E . Moreover, there is a kink around the ferroelectric transition temperature $T_{cf} = 56$ K. The kink is stronger for higher electric fields E and anharmonic spin-phonon interaction constants R .

It would be of interest to investigate the influence of cation substitution on the magnetic and dielectric properties in the doped magnetic relaxor ferroelectric CCS. This will be made in a next paper.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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