Phys. Status Solidi RRL **7**, No. 11, 1001–1004 (2013) / **DOI** 10.1002/pssr.201308093

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Multiferroism in the dielectric function of CuO

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Received 24 July 2013, revised 27 August 2013, accepted 27 August 2013
Published online 2 September 2013

Keywords multiferroics, dielectric function, magnetic fields, CuO

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The multiferroic properties of bulk CuO are manifested in the dielectric function which can be triggered by an external magnetic field h and by the temperature T. Within a microscopic model and a Green's function technique we have calculated the dielectric function $\varepsilon(\boldsymbol{k};T,h)$. At the magnetic phase transition temperature T_{N2} the dielectric function offers a pronounced anomaly. This kink disappears when the magnetic field is enhanced and $\varepsilon(\boldsymbol{k};T,h)$ decreases with increasing h-field. Both properties are indications for a strong magnetoelectric coupling in this material. The observation of multiferroism in CuO within an analytical approach is achieved by considering frustration and a linear magnetoelectric coupling.

Transition-metal oxides like CuO exhibit various intriguing phenomena such as high-temperature superconductivity and colossal magneto-resistance, see [1]. Recent extensive studies unveil that transition-metal oxides offer multiferroic properties, characterized by the coexistence of magnetism and ferroelectricity [2]. Copper oxide undergoes in zero magnetic field two successive magnetic phase transitions upon cooling from room temperature to near zero temperature. Neutron scattering experiments [3] show that in the low-temperature phase $T \le T_{N1} = 213$ K, the spin structure is collinear antiferromagnetic (AF1). In the temperature range $T_{N1} \le T \le T_{N2} = 230$ K the spin structure becomes non-collinear and the system offers a weakly incommensurate antiferromagnetic phase (AF2). For magnetic fields h along to the b-axis, a spin-flop transition is detected between $\mu_0 h = 11-13$ T at lower temperatures [4]. Moreover, CuO was found to be multiferroic at T_C where this transition temperature coincides with $T_{N2} = T_C$ [2]. Measurements of the dielectric function ε (DC) reveal that the magnetic transitions affect the dielectric properties. The temperature dependent DC exhibits a sharp peak structure at $T_{N2} = 230$ K suggesting a ferroelectric transition [2]. Such a direct coupling of a magnetic transition and a ferroelectric one is a strong indication for multiferroism. In addition, a smaller and stepwise anomaly appears at T_{N1}. This material has a very high transition temperature compared to all other known multiferroics [2]. The polarization, developed in the AF2 phase, can be reversed by applying an electric field. However, the mechanism for such a high ordering temperature is not well understood theoretically. The electric polarization was attributed to a spiral spin structure [3, 5] resulting from spin frustration whereas the high ordering temperature is believed to come from the strong exchange interactions [5]. Hence, CuO is a magnetically driven multiferroic material, where a non-collinear magnetic order within the range 213 K $\le T \le$ 230 K breaks the crystal inversion symmetry and hence induces ferroelectricity.

Zheng et al. [6] have shown that dielectric measurements can be a sensitive probe to detect the behavior of electrons and electron-spin interaction. CuO is a strongly electron-correlated system which was directly observed by dielectric anomalies at the magnetic phase transition temperature T_{N2}. Magnetoelectric effects (ME) in CuO have

been studied by measurements of magnetization, dielectric constant, and electric polarization with and without magnetic fields in Ref. [7]. Using polarized neutron diffraction Babkevich et al. [8] have observed an electric field control of chiral magnetic domains in the high-temperature multiferroic phase of CuO. Strong magneto-lattice coupling is observed in CuO [9–12]. Magnetic and dielectric properties are investigated also for CuO nanoparticles [13, 14].

The mechanism that causes the simultaneous emergence of ferroelectric and magnetic order in CuO is still under discussion. The modeling of the multiferroism is either based on the phenomenological Landau theory [4, 15] or first-principles calculations [16–19]. In the present paper, we propose a microscopic approach which is based on previous studies of CuO nanoparticles [20, 21]. The aim is to analyze multiferroic properties in the AF2 phase below $T_{N2} = 230$ K, because the bulk behavior of CuO is different from those observed in nanoparticles. Moreover, the bulk material offers a distinctive ferroelectricity characterized by a pronounced peak of the temperature dependent dielectric function. So, the model includes aside from magnetic interactions a magneto-strictive coupling to polar dielectric modes. The model is composed of an isotropic Heisenberg model including frustration and the mentioned magnetostrictive coupling of the magnetic spins to ferroelectric modes. Such a mode coupling theory leads to the polarization P. Here we follow the line given by [22] in explaining the properties of orthorhombic manganites $R\mathrm{Mn_2O_5}$. The ferroelectric subsystem is described by an Ising model in a transverse field which reflects the physical situation in mind adequately.

The microscopic model consists of three parts given by the Hamiltonian

$$H = H_{\mathrm{m}} + H_{\mathrm{f}} + H_{\mathrm{mf}} \ . \tag{1}$$

The Hamiltonian of the magnetic subsystem H_{m} is represented by the Heisenberg model including nearest neighbor ferromagnetic coupling $J > 0$ and next nearest antiferromagnetic coupling $\tilde{J} < 0$,

$$H_{\mathrm{m}} = -\tfrac{1}{2}\sum_{ij} J_{ij}\,\bar{S}_i \cdot \bar{S}_j - \tfrac{1}{2}\sum_{\langle ij\rangle} \tilde{J}_{ij}\,\bar{S}_i \cdot \bar{S}_j \ . \tag{2}$$

The sum over all next nearest neighbors is indicated by $\langle ij\rangle$. Due to the competition between ferromagnetic and antiferromagnetic order the magnetic subsystem is able to develop frustration if $|\tilde{J}| > |J|/4$ [23]. Obviously, the modeling of the magnetic subsystem by the Hamiltonian in Eq. (2) is a simplification. First-principle calculations [16–19] suggest that the magnetic behavior is characterized by four different coupling parameters within the spin Hamiltonian. Otherwise an analytical treatment with four different exchange coupling seems to be illusive. However, the simplified Hamiltonian Eq. (2) includes frustration as a feature of the magnetic subsystem. Notice that for a detailed study of the magnetic properties one has to include a single-ion anisotropy, too. However the influence of this anisotropy on the DC is small.

The ferroelectric behavior is modeled by the Ising model in a transverse field (TIM) which had been successfully applied for a large class of ferroelectric materials [24, 25]. The Hamiltonian reads

$$H_{\mathrm{f}} = -\Omega \sum_i B_i^x - \tfrac{1}{2}\sum_{ij} J'_{ij} B_i^z B_j^z \ . \tag{3}$$

In the same sense as in the magnetic subsystem the model is a simplification of the real situation. Here the spin-like operator B_i^z characterizes the two alignments of the ferroelectric unit at the lattice point i. Notice that the introduction of spin operators is only a mapping and has nothing to do with real spins. The interaction between the oriented dipoles at adjacent lattice sites is denoted by J'_{ij}. Whereas the conventional Ising model has no own dynamics the model defined by Eq. (3) reveals a flip dynamics characterized by the first term with strength Ω. Even the pseudo-spin operator B^x models the flip process of the ferroelectric units. Because the eigenvalues ± 1 of B_i^z can be understood as positioning in a double well potential the parameter Ω is sometimes called tunneling frequency. In the ordered phase both mean values $\langle B^x\rangle$ as well as $\langle B^z\rangle$ are non-zero. Therefore the Hamiltonian in Eq. (3) is rotated by an angle θ in the xz-plane. The rotation angle θ is determined by the requirement $\langle B^{x'}\rangle = 0$ in the new frame.

The last term in Eq. (1) describes the coupling between the magnetic and the ferroelectric subsystems. We propose a ME coupling of the form

$$H_{\mathrm{mf}} = -g \sum_{ijl} B_i^z \boldsymbol{S}_j \cdot \boldsymbol{S}_l \ . \tag{4}$$

The parameter g is a measure for the coupling strength between the magnetic and the electric order parameters. The ME coupling in CuO should be invariant with respect to spatial and time inversions. Our coupling follows the spirit of the mesoscopic approach proposed in [5]. On that level the coupling of the polarization field $\boldsymbol{P}$ and the magnetization field $\boldsymbol{M}$ has the form $\boldsymbol{P}\cdot\boldsymbol{M}(\nabla\cdot\boldsymbol{M})$. Our coupling in Eq. (4) is likewise linear in the pseudo-spin reflecting the polarization and quadratic in the magnetic spins. The summation over nearest neighbor is related to the ∇-operator in a mesoscopic calculation. Formally, the coupling constant g should be a pseudo-scalar.

The dielectric function $\varepsilon(\boldsymbol{k}, E)$ is related to the Green's function which obeys the following equation [26]:

$$\left[\left(\frac{\Lambda}{\varepsilon(\boldsymbol{k},E)-1}\right)_{\alpha\gamma} + \Lambda\frac{k_\alpha k_\gamma}{k^2}\right] G^{\gamma\beta}(\boldsymbol{k},E) = \delta_{\alpha\beta} \ , \tag{5}$$

with $\Lambda = 4\pi Z^2/v$. The Green's function is a 3×3 matrix. In particular, the dielectric function $\varepsilon(\boldsymbol{k}, E)$ of the system is related to the longitudinal anti-commutator Green's

function $G^{zz}(\boldsymbol{k}, E) = \langle\langle B^z_{\boldsymbol{k}}; B^z_{-\boldsymbol{k}}\rangle\rangle$ which is calculated as

$$G^{zz}(\boldsymbol{k},E) = \frac{2\langle B^z(\boldsymbol{k})\, B^z(-\boldsymbol{k})\rangle\,(E^2 - (E^f(\boldsymbol{k}))^2 + 2iE\gamma^{11})}{(E + i\gamma^{33})\,(E^2 - (E^f(\boldsymbol{k}))^2 + 2iE\gamma^{11}) - E(\varepsilon^{13})^2}\,. \tag{6}$$

Here ε^{13} describes the coupling between the transverse and the longitudinal modes, whereas the transverse γ^{11} and the longitudinal damping parameters γ^{33} in Eq. (7) can be found using a method proposed in [27]. In order to determine the complex dielectric function $\varepsilon(\boldsymbol{k}, E)$ we have to separate the related Green's function according to Eqs. (5) and (6) in the real and imaginary part. From Eq. (5) we obtain $\varepsilon(\boldsymbol{k}, E)$ which can be analyzed for different parameters. In order to obtain the total excitation energy of the system and their damping one has to calculate additively the following Green's function $G(\boldsymbol{k}, \omega) = \langle\langle B^+_{\boldsymbol{k}}; B^-_{-\boldsymbol{k}}\rangle\rangle$, where B^+ and B^- are the spin-$\frac{1}{2}$ ladder operators in the rotated system. The excitation energy is the pole of $G(\boldsymbol{k}, \omega)$. It results

$$\begin{aligned} E_f(\boldsymbol{k}) = {} & 2\Omega\sin\theta \\ & + \frac{1}{2}P\cos^2\theta J'^{\mathrm{eff}} - \frac{1}{4}P\sin^2\theta J'^{\mathrm{eff}}(\boldsymbol{k}) \\ & - \frac{1}{NP}\sum_q \Big(\cos^2\theta J'^{\mathrm{eff}}(\boldsymbol{k}-\boldsymbol{q}) \\ & - \frac{1}{2}\sin^2\theta J'^{\mathrm{eff}}(\boldsymbol{q}) \Big) \langle B^-_q B^+_q\rangle\,. \end{aligned} \tag{7}$$

From that Green's function and the related excitation energy in Eq. (7) we find the relative polarization $P(T)$ which is directed along the b-direction

$$P = \frac{1}{2N}\sum_k \tanh\frac{E^f(\boldsymbol{k})}{2k_{\mathrm{B}}T}\,. \tag{8}$$

The result for the energy spectrum of the multiferroic system in Eq. (7) offers that the coupling constant J' between the pseudo-spins, introduced in Eq. (3), is renormalized due to the interaction between the electric and magnetic subsystems. Moreover the renormalized coupling is modified by corresponding correlation functions. The modified interaction reads $J'^{\mathrm{eff}} = J'_0 + 2g(\langle S^-_q S^+_q\rangle + \langle S^z_q S^z_q\rangle)$. Notice that the random phase approximation leads to $\langle S^z_q S^z_q\rangle \simeq \langle S^z_q\rangle^2$. In a similar manner one can calculate the magnetization $M = \langle S^z\rangle$ which is related to the Green's function of the magnetic subsystem defined by $g(\boldsymbol{k}, E) = \langle\langle S^+_{\boldsymbol{k}}; S^-_{\boldsymbol{k}}\rangle\rangle$ with the related ladder spin operators $S^{\pm}$.

In order to investigate the dielectric behavior originated from the magnetic ordering in CuO we consider the temperature dependence of the dielectric function in b-direction as well as the dependence on a magnetic field [2]. As parameters we have chosen $J = 75$ K, $\tilde{J} = -62$ K, $J' = 53$ K, $g = 50$ K. The exchange parameters J are chosen by their relation to the phase transition temperatures.

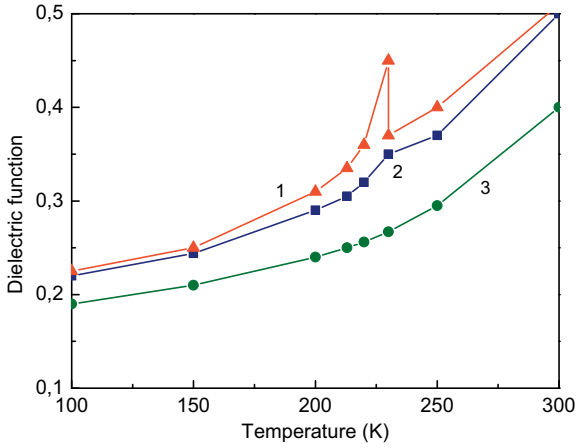

Figure 1 Temperature dependence of the dielectric function $\varepsilon \parallel b$ of CuO: (1) for $h \parallel c = 10$ Oe, $g = 50$ K; (2) for $h \parallel c = 10$ Oe, $g = 10$ K; (3) for $h \parallel c = 1000$ Oe, $g = 50$ K.

The numerical results are shown in Fig. 1. At first let us discuss the temperature dependence of the DC on an external magnetic field h. For that aim the Hamiltonian in Eq. (1) is completed by a term of the form $-\mu_{\mathrm{B}}\mu_0 h \sum_i S^z_i$ which describes the coupling to the magnetic field h. The influence of the field is the largest one in case $h \parallel c$. It can be seen in Fig. 1 (curve 1) for $h = 10$ Oe that near to the transition temperature $T_{\mathrm{N2}} = 230$ K the dielectric function shows an anomaly. The sharp change in the dielectric function at this magnetic transition demonstrates clearly the pronounced ME coupling in CuO. This behavior is in good qualitative agreement with the experimental data of Kimura et al. [2] and Wang et al. [7]. Remark that our study reveals no anomaly within the dielectric function in a-direction. In case the ME coupling parameter g in Eq. (4) is reduced, the peak at T_{N2} is smaller (see curve 2). If the ME coupling vanishes, i.e. $g = 0$, the peak disappears. From here we conclude that the magnetic ordering affects the dielectric behavior. One feature of multiferroic material is the possibility that the dielectric properties can be influenced by an external magnetic field. Likewise the magnetic behavior can be triggered by an electric field. Hence we have calculated the dielectric function for a magnetic field $h \parallel c = 1000$ Oe. The result is depicted as curve 3 in Fig. 1. One observes that ε is suppressed and the dielectric anomaly disappears when the magnetic field becomes stronger. Because an external field couples directly to the magnetic order parameter, it is easy to change the ferromagnetic moment and therefore produce changes in the dielectric constant. Wang et al. [7] reported that both the dielectric constant and the polarization offer only slight changes in a magnetic field of $\mu_0 h = 7$ T. Such a suppression of dielectric properties by an external magnetic field is also reported in other multiferroics, for example in orthorhombic $R\mathrm{MnO_3}$ [28], hexagonal $R\mathrm{MnO_3}$ [29] and in the new multiferroic material $\mathrm{CuBr_2}$ [30]. To our knowledge there is a lack of experimental results concerning the influence

of external magnetic fields on the dielectric properties of CuO.

To extend the model one can include spin–phonon interaction [20] in the bulk material, too. The recent analytical outcome of the phonon spectrum of CuO nanoparticles [21] should be a good motivation for doing that. Especially, the results for nanoparticles are in agreement with the experimental data obtained in [11, 12, 31]. Generally, the occurrence of spin–phonon interaction in CuO is experimentally suggested by [11–13]. The spin–phonon coupling in the bulk gives rise to a stronger kink at T_{N2} and we expect also a small influence on T_{N1}. Moreover the magnetic transition is also manifested by an anomaly in the phonon energy near to T_{N2} and the damping of the phonon mode is related to the full width at the half maximum of the Raman lines. Simultaneously the spin–phonon interaction should have an impact on the magnetic properties in CuO as demonstrated recently [20]. A second aspect in modifying the present model is the analysis of the dielectric function for CuO nanoparticles. Here we expect a more pronounced peak at T_{N2} due to surface effects.

In conclusion, we have proposed a microscopic model in order to describe the multiferroic properties of CuO bulk material. To characterize the multiferroism the dielectric function $\varepsilon(\boldsymbol{k}, E)$ is calculated. The approach is based on a Green's function technique of the underlying Hamiltonian including ME coupling and frustration. The dielectric function exhibits an anomaly at the magnetic phase transition temperature T_{N2}. In particular, we demonstrate that this anomaly in $\varepsilon(\boldsymbol{k}, E)$ can be triggered by an external magnetic field. The anomaly can be suppressed by increasing the magnetic field which is a strong indication for a ME coupling. The temperature and magnetic field dependence of ε reveals the mutual effect between magnetic alignment and dielectric properties. The proposed model is in agreement with experimental data for CuO. The model could be applied to describe the multiferroic properties of the other new multiferroic materials as $CuBr_2$ [30] and $CuCl_2$ [32].

Acknowledgements One of us (S.G.B.) acknowledges support by the International Max Planck Research School for Science and Technology of Nanostructures in Halle.

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