Energy scale of dielectric coupling in antiferromagnetic insulators

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Abstract

To probe the energy of dielectric coupling between the dipole chains and the quasipolarons based on extension of the polaron concept, dielectric and magnetic properties of antiferromagnetic insulators, namely Ca₄₋ₓCuxTi₄O₁₂ (x = 3, 2 and 1), are investigated at different temperatures. The energy is estimated larger than 56 meV of the dipole interaction energy, but smaller than 88 meV of the dipole-chain thermal activation energy which is for the Dissado-Hill type dielectric relaxation. In particular, the quasipolaron ingredient is at least 28 meV of the total superexchange interaction which bond one single titanium ion of the dipole chain with four quasipolarons. Then, the energy of the coupling is in the range from 84 meV to 88 meV. The experimental observation, suggests the dielectric coupling may provide an approach to obtain large permittivity in strongly-correlating systems of antiferromagnetic insulators.

The coupling in strongly correlated systems, may manifest itself as an important part of diverse physical phenomena, such as the trimeron-phonon coupling for the Verwey transition in the metallic ferrimagnet Fe₃O₄ [1], and the electron-phonon one for the wide and direct band gap in the polar semiconductor GaN [2]. As the carrier of these coupling, 3d electrons may show different forms of electron quasiparticles, i.e. the trimeron (three-site polarons) for the Fe-3d electron and the Fröhlich polarons for the Ga-3d electron, respectively. The polaron is, in crystalline solids, the electron interacting with a quantized bosonic field, which localizes or moves in an ordered or disorder system, polarizes its surroundings, and dresses itself with bosonic excitations (phonons, electronic spin/charge/orbital fluctuations and so on). As one sign of the polarized lattice, the coupling of an electron to a polar lattice is expressed in terms of a dielectric continuum. For example, the Fröhlich polaron coupling constant, $\alpha$, includes the defined permittivity, $\varepsilon^*$, i.e. $\alpha = |e^2/\tilde{\varepsilon}^*|/\hbar\omega_{LO}$, where $\varepsilon$ is the charge of the electron, $\varepsilon_0$ is the permittivity of free space, $\hbar$ is the reduced Planck constant, $\omega_{LO}$ is the longitudinal optic (LO) mode, and $[e^2/(8\pi\varepsilon_0\tilde{\varepsilon}^*)]$ is the Coulomb interaction strength. $\tilde{\varepsilon}^*$ is in terms of $\tilde{\varepsilon}^* = 1/\varepsilon_{\infty} - 1/\varepsilon_0$, where $\varepsilon_{\infty}$ is the highest frequency permittivity.

By the phonon-related coupling, different forms of polarons deform local or overall lattices for the dielectric polarization and the permittivity, partly for ion polarizations can follow polaron motion if the motion is sufficiently slow [3]. In an ionic crystal or a polar semiconductor, Fröhlich polarons are with the polarization carried by the LO phonons, which is represented by a set of quantum oscillators with the long-wavelength LO-phonon frequency, and the interaction between the charge and the polarization field is linear in the field. In the manganites, the small polaron induces the lattice polarization, which is essentially confined to a unit cell, and may pair with oxygen holes into heavy bipolarons in the paramagnetic phase and their magnetic pair breaking in
the ferromagnetic phase. In some insulators or semiconductors, the electronic polaron is induced as an extension of the polaron concept by considering the interaction between a carrier and the excition field. More experimental and theoretical investigations have been required to provide the convincing evidence for their occurrence, and new theoretical concepts and experimental methods still need to develop. So far, these quasiparticles are considered to couple only with bosonic excitations, and however, coupled with other dielectric polarization species have been never reported. The relevant experiments are rare. Such case may be demonstrated by the coexistence of two dielectric species, i.e. the polaron-like polarization species have been never reported. The relevant experiments are rare. Such case may be.

Following the suggestion of the single electron like the polaron by Anderson in the theory of super-exchange interaction [7], we name the electron as quasi-polaron, and above TN, a collective of them may be electrically excited to behave as the other dielectric species. The strongly correlated system of the ionic dipole chains and the quasi-polarons, lays a ground for the self-consistent quantum picture, comprehensively for dielectric, antiferromagnetic, optical and photo-related phenomena [8]. The intrinsic dielectric coupling between these two dielectric species is revealed above 140 K, in the process of the quantum modulation on the B-site transition-metal subarray [4].

The dielectric coupling sign is, in the impedance spectrum, revealed by the relation between the magnitude of the real part of complex dielectric function, ε’ (the scientific form of permittivity), and the stoichiometric proportion of Cu ions, x, i.e. the population ratio of the quasi-polaron species. When the x is decreased from 3, to 2, and then to 1, the value of ε’ is reduced by one order of magnitude during each step, as shown in figure 2(a). The relation has been formulated as the following [4]:

\[ \lg \varepsilon' = x + 1 \]  

(1)
where \( \int \) is the integral function. The loss tangent, \( \tan \delta \), smaller than 1, confirms these materials are insulators, as shown in figure 2(b), where \( \tan \delta \) is the ratio of the imaginary part of complex dielectric function, \( \varepsilon'' \), to \( \varepsilon' \). After the key dielectric effect of grain boundaries, twinning boundaries, A-site Ca/Cu atomic disorders and other defects is excluded [5, 9, 10], the binary dielectric polarizing species of the ionic dipole chain and the electron quasi-polaron, vary in the response to the frequency of excited A. C. electric field, and therefore, the complex dielectric plot at the low field is necessary to distinguish them. As shown in figure 2(c), the parallel-dipole-orientation branch is triggered by the electric excitation [9], and the external inversion-symmetry-restriction breaking of the dipole chains results into a non-zero net polarization above a high frequency of \( \sim 10^{4.6} \) Hz. Notably, the dielectric polarization of quasi-polarons takes the response at lower frequencies. With the decreased population, so is the maximum response frequency of the quasi-polarons (MRS). Because of the less CaCu\(_3\)Ti\(_4\)O\(_{12}\) ingredient, the MRS of Ca\(_2\)Cu\(_2\)Ti\(_4\)O\(_{12}\) is smaller but close to that of CaCu\(_3\)Ti\(_4\)O\(_{12}\), while that of Ca\(_3\)CuTi\(_4\)O\(_{12}\) is much smaller than others. Simultaneously by the dielectric coupling, the contribution of dipole chains to the value of \( \varepsilon'' \) is depressed. At the room temperature of 300 K, the dielectric coupling is, at least, against the thermal destruction of \( k_B T \) about 26 meV, where \( k_B \) is the Boltzmann constant and \( T \) is the thermodynamic temperature. We have estimated the interaction energy among dipoles in one dipole chain about 56 meV down

Figure 1. XRD pattern, TEM and SEM pictures of CaCu\(_3\)Ti\(_4\)O\(_{12}\) (a, d and g), Ca\(_2\)Cu\(_2\)Ti\(_4\)O\(_{12}\) (b, e and h) and Ca\(_3\)CuTi\(_4\)O\(_{12}\) (c, f and i), respectively. The inset in figure 1(a) shows the crystal and \( d \) orbital structures of CaCu\(_3\)Ti\(_4\)O\(_{12}\), with Ca (orange), Cu (green), O (red) and Ti (blue) ions. Unpaired spins of quasi-polarons order at the orbitals, pointing in the (111) or (T1T) directions and giving rise to a spin structure. The green line in figure 3(c) signifies the dielectric coupling between ionic dipole chains and electron quasi-polarons.
to 0 K [11]. Thus, the energy of the coupling should be larger than 56 meV, otherwise the depression may not be made.

To detail the quasipolaron ingredient of the coupling, we also investigate the temperature-dependent dielectric responses at different frequencies, and the magnetic responses under 100-oersted (100-Oe) static magnetic field after the zero-field cooling is applied. When the temperature is cooled from 300 K, the 100-fold drop of the $\varepsilon'$ value without a long-range structural transition is around 100 K in CaCu$_{3}$Ti$_4$O$_{12}$, accompanying with the Dissado-Hill type dielectric relaxation, as typically shown in figure 3(a). The dielectric relaxation units are the dipole chains. For these dipole chains are independent on each other, we use the Arrhenius Law of the single body approximation to deduce the thermal activation energy about 88 meV in CaCu$_3$Ti$_4$O$_{12}$. Ca$_2$Cu$_2$Ti$_4$O$_{12}$ and Ca$_3$CuTi$_4$O$_{12}$ shows the same dielectric relaxation temperature as that of CaCu$_3$Ti$_4$O$_{12}$, as shown in figure 3(b) (dash dot line), and therefore, the quantum modulation does not change, by the coupling, the thermal activation process of dipole chains, and then, the basic characters of dipole chains, including the

**Figure 2.** The plot of $\varepsilon'$ versus $f$ (a), tg$\delta$ versus $f$ (b) and complex dielectric plot (c) at 300 K.
length, the mutual independence, the interaction energy, the distribution. Thus, we estimate the energy of the coupling is smaller than 88 meV.\(^5\) However, less quasipolarons involve into the dynamic electrical-field response of dielectric polarization, and the value of \(\tan\delta\) is decreased. As shown in figure 3(c), all of three strong correlating systems show the same \(T_N\) of magnetic moment (M), revealing the same strength of the superexchange interaction. In CaCu\(_3\)Ti\(_4\)O\(_{12}\), the superexchange between the copper spins is promoted via the titanium ions rather than via the usual oxygen path\(^{12}\). The two superexchange interactions pass through one titanium ion, and the total strength of the superexchange interaction is about 28 meV. Thus, the quasipolaron ingredient of the coupling is, at least, 28 meV. At present, the energy of dielectric coupling between the dipole chains and the quasipolarons is the key for the large permittivity, other antiferromagnetic insulators with similar crystallinity and compositions may have the similar or more favorable energy of dielectric coupling. In these

\[5\]

Figure 3. The plot of \(\varepsilon'\) versus \(T\) (a), \(\tan\delta\) versus \(T\) (b) at different frequencies and \(M\) versus \(T\) (c) at 100 Oe of the magnetic field in a wide temperature range. Spin structure of quasipolarons in CaCu\(_3\)Ti\(_4\)O\(_{12}\). The copper (green) and calcium (orange) atoms of the lower right front eighth of the unit cell (the inset of figure 1(a)) are shown. The TiO\(_6\) octahedron is neglected for clarity. Each quasipolaron of \(\text{Cu}^{2+}\) ion carries a spin, pointing in the (111) or (\text{\overline{1}}1\text{\overline{1}}) direction. \(J_1, J_2,\) and \(J_3\) are the exchange integrals between nearest, next-nearest and third-nearest neighbors.
transition metal oxides with Cu, Fe, Ni and etc., the inversion symmetry is not necessarily restricted, but the local Jahn-Teller distortion are required for local dipoles which can be excited to break the symmetry for the macroscopic polarization. Meantime, the symmetry of time inversion is broken.

In conclusion, we theoretically extend the concept of polaron to that of quasi-polaron, and experimentally estimate the energy scale of a dielectric coupling, which has never been reported before, since the discovery of dielectrics. The estimation opens a door to investigate different types of dielectric coupling in two, three and more dielectric species in strongly-correlating systems of giant or supergiant permittivity antiferromagnetic insulators.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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