Orbital glass induced by 2D antiferromagnetic fluctuations in Eu_2CuO_4

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A low-frequency dispersion of the permittivity which is characteristic of structural glasses [E. Courtens, Phys. Rev. B **33**, 2975 (1986)] has been observed in an insulating single crystal of Eu_2CuO_4 in the temperature range 120–300 K. A model in which the glassy behavior arises in the orbital magnetic system of Jahn–Teller Cu^{2+} ions is proposed. This behavior arises because the interaction of tetragonal magnetic doublets through the 2D AFM spin subsystem is a variable-sign long-range interaction. It is suggested that this interaction leads, by virtue of a transition to chaos, to a glassy behavior even in an ordered system.

A study of the magnetic susceptibility of Eu_2CuO_4 single crystals above the temperature of the 3D antiferromagnetic (AF) ordering ($T_N=165$ K) has revealed a wide region (along the temperature scale) of 2D AF spin fluctuations in CuO_2 planes.[2] Since the Cu^{2+} ions are Jahn–Teller ions, and since there is the possibility that the Jahn–Teller and spin subsystems interact with each other, we undertook a study of the permittivity ϵ in the temperature range in which the 2D AF spin fluctuations exist.

The measurements were carried out over the frequency range from 70 Hz to 1 MHz and over the temperature range 4.2–400 K. Insulating single crystals of the highest quality were selected for these measurements ($\sigma < 10^{-9}$ Ω/cm at 300 K). Since the crystals grow as thin platelets with large plane perpendicular to the c axis, it was possible to measure only the component of the permittivity transverse with respect to this plane (ϵ_c). It can be seen from Fig. 1 that at low temperatures, at which there is a 3D AF order, the real part of the permittivity ($\mathrm{Re}\,\epsilon$) is independent of the temperature. Near T_N ($T>120$ K), $\mathrm{Re}\,\epsilon$ begins to rise. At $T\sim 250$ K a peak is observed in $\mathrm{Re}\,\epsilon$ at low frequencies. As the temperature is raised further, there is a transition to a new constant value. There is a pronounced low-frequency dispersion of ϵ. The values of the loss tangent in the dispersion region are fairly small: $\mathrm{Re}\,\epsilon \tan\delta \sim 0.01$ at the temperatures at which $\mathrm{Re}\,\epsilon$ begins to rise and $\tan\delta\sim 0.3$ at the temperature at which $\mathrm{Re}\,\epsilon$ becomes constant. The dispersion curves in Fig. 1 are similar to those which have been observed in spin glasses[3] and structural glasses.[1] We believe that in our case, as usual in glassy systems, the low-frequency dispersion stems from the presence of relaxation oscillators with a wide variety of relaxation times ($\tau_{\min} \ll \tau \ll \tau_{\max}$). However, a more careful analysis of the situation reveals that there

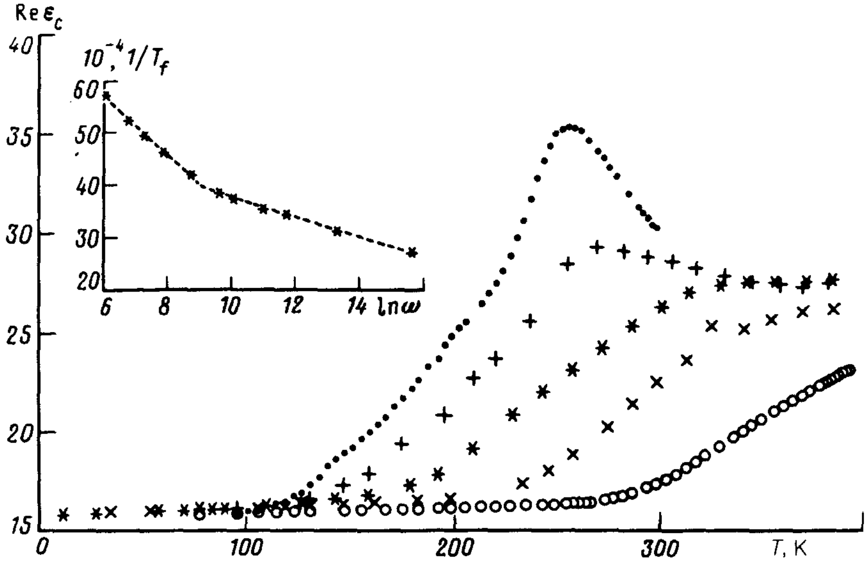

FIG. 1. Temperature dependence of Re ϵ_c at several fixed frequencies. ●—70 Hz; +—230 Hz; $*$=1 kHz; ×—20 kHz; □—1 MHz. The inset shows $1/T_f$ versus ln ω.

are also certain features which distinguish the pattern here from the usual pattern for glasses.

We denote by T_f the temperature of the peak of the derivative of Re ϵ with respect to T at a fixed frequency ω. Analysis of the T dependence of Re ϵ (Fig. 1) shows that we have $\tau=1/\omega=\tau_0\cdot\exp(E_A/kT_f)$ and that there are two linear regions (see the inset in Fig. 1) on the plot of $1/T_f$ versus lnω. The change in slope occurs at the values $T_f=T_{cr}=250$ K and $\tau=\tau_{cr}=2\times10^{-4}$ s. The values of the parameters E_A and τ_0 are $-E_A=0.13$ eV, $\tau_0=1.2\times10^{-7}$ s ($120\text{ K}<T<250\text{ K}$) and $-E_A=0.37$ eV, $\tau_0=4\times10^{-14}$ s ($T>250$ K). Glassy systems ordinarily exhibit only a single linear region. The value of E_A at low temperatures is smaller than that at high temperatures; the value of τ_0 changes by several orders of magnitude as we go from the low-temperature region to the high-temperature region.

We can find the density of relaxation-oscillator states,[1,3] $-g(1/\omega,T)$, by analyzing the frequency dependence of Re ϵ. If there exists a wide set of relaxation times in the system ($\tau_{min}\ll\tau\ll\tau_{max}$), we find, using the Kramers–Kronig relations,[1,3]

$$\epsilon=1+4\pi\chi,\quad \chi=\Delta(y)+i\pi/2\alpha\Delta'(y),\quad y=-\alpha\ln(\omega\tau_0). \tag{1}$$

Relation (1) is valid under the conditions $y\propto 1$ and $\alpha\ll 1$. The quantity $\alpha\Delta'(y)$ is $g(1/\omega,T)$. Near the measurement frequency ω_0, an expansion (1) yields

$$\chi(\omega)\simeq\Delta(y_0)-\alpha\Delta'(y_0)(\ln\omega/\omega_0-i\pi/2),\quad y=-\alpha\ln(\omega_0\tau_0). \tag{2}$$

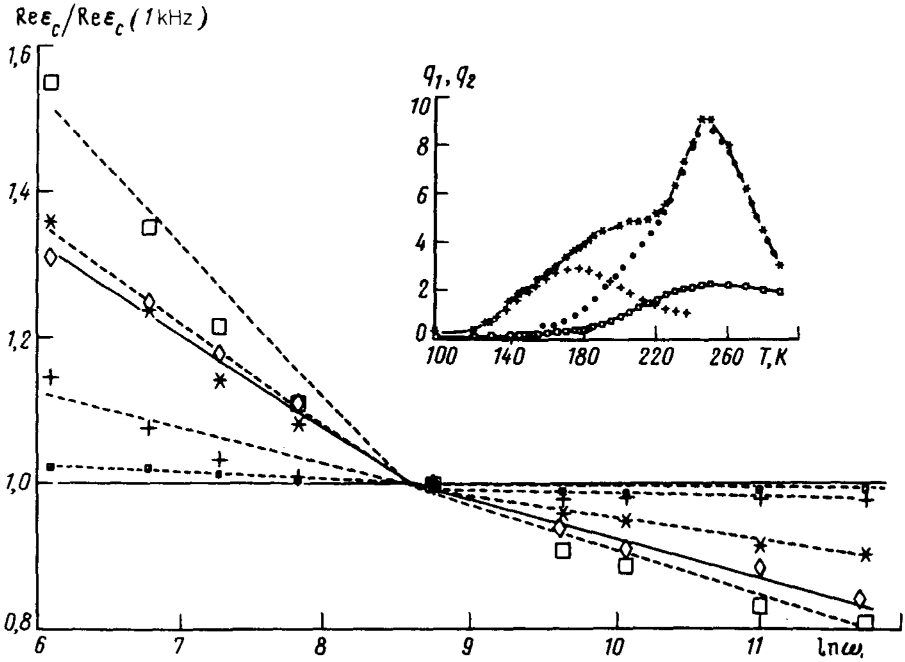

FIG. 2. Anomalous dispersive part of the permittivity Re ϵ_c /Re ϵ_c (1 kHz) as a function of ln ω at several fixed temperatures. ■—100 K; +—150; *—200; □—250; ◇—290 K. The inset shows the temperature dependence of g_1 and g_2.

Glassy systems usually exhibit a linear dependence of Re ϵ on lnω. According to Eqs. (1) and (2), this linearity means that the density of states of the relaxation oscillators, $-g(1/\omega,T)$, remains constant as $1/\omega$ varies. In our case (Fig. 2), there are two regions of a constant density of states: $g_1-[(1/\omega)_{\rm cr}<1/\omega<(1/\omega)_{\rm max}]$ and $g_2-[(1/\omega)_{\rm min}<1/\omega<(1/\omega)_{\rm cr}]$. There is an abrupt jump in this density at $1/\omega=1/\omega_{\rm cr}=2\times10^{-4}$ s. The inset in Fig. 2 shows the temperature dependence of g_1 and g_2 (the upper and lower curves, respectively). The upper curve can be decomposed in a natural way into two curves, peaking at $T=165$ K and $T=250$ K. The first peak corresponds to T_N, as we see, while the second corresponds to the value $T_f=T_{\rm cr}$ in Fig. 1. In addition, the values $1/\omega_{\rm cr}=2\times10^{-4}$ s found from the data in Figs. 1 and 2 are essentially the same. There is accordingly a critical relaxation time in our glassy system.

Analysis of the experimental data on the temperature dependence and frequency dependence of Re ϵ shows that the stoichiometric and structurally ordered Eu_2CuO_4 single crystal exhibits a glassy behavior typical of disordered, frustrated systems (with a variable-sign competing interaction). We believe that the glassy properties are a manifestation of the Jahn–Teller subsystem of Cu^{2+} ions and a consequence of an interaction between the spin and Jahn–Teller subsystems.

The spin subsystem (S) of copper is a quasi-2D Heisenberg exchange AF with an exchange constant J_1 (for La_2CuO_4, we have[4] $J_1 \sim 1500$ K). The weak interplane exchange leads to a 3D AF order with[2] $T_N = 165$ K. At $T > T_N$, the large value of J_1 and the value $S = 1/2$ lead to the existence of 2D AF spin fluctuations with a large correlation radius[4] $\xi \sim a \cdot \exp(2\pi\rho_s/kT)$ over a broad temperature range. Here a is the lattice constant, and ρ_s is the spin stiffness $(2\pi\rho_s \sim J_1)$. At $T \sim T_N$ we have $\xi \sim 10^3\, a$.

Let us examine the Jahn–Teller system of Cu^{2+} ions. The compound Eu_2CuO_4 has a tetragonal structure of the $T'(I4/mmm)$ type.[5] To explain the experimental data, we adopt the following assumptions.

1. The ground state of the orbital subsystem of copper is the tetragonal doublet Γ_5^t (the notation is that of Ref. 6), which arises from the cubic triplet $\Gamma_5(t_{2g})$. The orbital doublet Γ_5^t is known to be magnetic. A corresponding hypothesis was adopted in Ref. 7 regarding the ground state of the copper orbital system for La_2CuO_4.

2. The spin–orbit (SO) interaction of the Cu^{2+} ions is far stronger than the interaction of orbitals with phonons.

These assumptions lead to an analog of the Jahn–Teller effect involving magnons, with a replacement of vibronic (i.e., orbital–phonon) states by spinon (i.e., orbital–magnon) states.

If we project the SO interaction operator -**LS**- onto the basis of the tetragonal doublet, we obtain the interaction -$\sigma^z S^z$-, where the matrix σ^z operates in the space of magnetic orbitals with projections $L_z = \pm 1$. This circumstance distinguishes these states from the Γ_3 doublet, in which corresponding matrices formally reflect the twofold degeneracy.

The interaction Hamiltonian is

$$H = \sum_{ij} J_{1ij} \mathbf{S}_i \mathbf{S}_j + \lambda \sum_i S_i^z \sigma_i^z, \tag{3}$$

where $\mathbf{S}_i$ is the spin of site i, J_{1ij} is the quasi-2D spin AF exchange (the constant J_{1ij} is zero except for nearest neighbors), and λ is the spin–orbit interaction constant. We assume $J_{1ij} > \lambda$, and we assume that perturbation theory is legitimate.

The effective Hamiltonian for the σ subsystem is

$$H_{\text{eff}}^{\sigma} = \lambda \sum_i \langle S^z \rangle_i \sigma_i^z + \lambda^2 \sum_{(ij)} K_{ij}^{zz} \sigma_i^z \sigma_j^z, \tag{4}$$

where $K_{ij}^{zz} = \langle S_i^z S_j^z \rangle - \langle S_i^z \rangle \langle S_j^z \rangle$ is the correlation function of the S subsystem, and (ij) means a summation over all pairs of lattice sites. The first sum in (4) describes the influence of the effective field $h_i^z = \lambda \langle S_i^z \rangle$ on the σ subsystem; the second describes the interaction of the σ subsystem through fluctuations of the S subsystem. Let us analyze the latter interaction. Following Ref. 4, we write $S_i^\alpha = (-1)^{d_i} \Omega_i^\alpha$, where Ω_i^α is a component of the AF order parameter; $d_i = 0, 1$, depending on which of the two AF sublattices contains site i; and

$$\langle\Omega_i^\alpha\Omega_j^\beta\rangle=\delta_{\alpha\beta}L(r_i-r_j),\quad K_{ij}^{zz}=(-1)^{d_i+d_j}L(r_i-r_j). \tag{5}$$

According to Ref. 4 we have $L(r_i-r_j)\sim(r_{ij})^{-1/2}\exp(-r_{ij}/\xi)$, $r_{ij}=r_i-r_j$, and

$$H_{\rm eff}^z=\sum_i h_i^z\sigma_j^z+\sum_{(ij)} J_{2ij}^{zz}\sigma_i^z\sigma_j^z. \tag{6}$$

Here $H_{\rm eff}^z$ is the effective Hamiltonian of the Jahn–Teller subsystem as the result of the orbital-magnetron interaction. On the one hand, the interaction $J_{2ij}^{zz} = \lambda^2(-1)^{d_i+d_j}L(r_{ij})$, is a long-range interaction; on the other, it changes sign each lattice constant. In addition, the molecular field $\Sigma J_{2ij}^{zz}\langle\sigma_j^z\rangle$ is quite distorted in comparison with the value J_{2ij}^{zz}, because of the long range of the J_{2ij}^{zz} interaction. A variable-sign (frustrating), long-range interaction thus arises in the σ subsystem, because of the 2D *AF* fluctuations with a large correlation radius in the *S* subsystem.

In random systems it is specifically a variable-sign interaction which leads to a glassy behavior. In our case, we are dealing with a crystal with an ordered Jahn–Teller subsystem, but with a specific variable-sign, long-range interaction. Ordered systems with a variable-sign but short-range interaction have been studied actively in recent years.[8,9] Some fairly complex phase diagrams have been found, but no spin glass.

We believe that ordered frustrated systems with a long-range interaction undergo a transition to chaos. For this reason, a glassy behavior may be exhibited by ordered systems of this sort. Physically, this suggestion seems quite natural, although it does require some additional arguments, which might be found, in particular, by numerical simulation. The transition to chaos in ordered frustrated systems (of a different type) has been studied previously.[10,11]

Let us look at our experimental situation. As a result of the local Jahn–Teller effect of the orbital-magnon type, two-level systems arise for degenerate orbital doublets with different values of $\langle\sigma^z\rangle$. These two-level systems result from an interaction with phonons. The slight orbital-lattice interaction causes the displacements of the Cu^{2+} ions (and, correspondingly, the permittivity which we measured) to depend on the values of $\langle\sigma^z\rangle$. In our case we have $\lambda\langle S^z\rangle > J_2^{zz}\langle\sigma^z\rangle$ in the low-temperature region. The effective field $\lambda\langle S^z\rangle$ suppresses the glassy state[3] and leads to a "staggered-field" state in the σ subsystem. As $T\to T_N$, we have $\langle S\rangle\to 0$, and the glassy properties of the Jahn–Teller orbital subsystem become apparent. They persist at $T>T_N$. At $T\gg T_N$, the interaction range and the size of the molecular field, $J_2^{zz}\langle\sigma^z\rangle$ decrease, and the glassy behavior of the Jahn–Teller orbital subsystem should disappear.

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