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## Origin of apparent colossal dielectric constants

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Experimental evidence is provided that colossal dielectric constants  $\epsilon' \geq 1000$ , sometimes reported to exist in a broad temperature range, can often be explained by Maxwell-Wagner-type contributions of depletion layers at the interface between sample and contacts or at grain boundaries. We demonstrate this on a variety of different materials. We speculate that the largest intrinsic dielectric constant observed so far in nonferroelectric materials is of order  $10^2$ .

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Materials exhibiting a colossal dielectric constant (CDC)  $\epsilon' > 10^3$  have recently gained considerable attention. CDC behavior is of technical importance for applications using high- $\epsilon$  electronic materials, such as random access memories based on capacitive elements. Fundamental interest was initiated by the observation of CDC behavior in some high- $T_c$  parent compounds.<sup>1,2</sup> Indeed, CDC behavior may indicate a colossal polarizability, which was invoked in early polaronic and bipolaronic models as a possible mechanism for high- $T_c$  superconductivity.<sup>3</sup> During the last decade, similar observations of CDC behavior have been reported in an increasing number of materials, such as transition-metal oxides.<sup>4-6</sup>

Large dielectric constants are expected for ferroelectrics in a narrow temperature range close to  $T_c$  or for systems with hopping charge carriers yielding a dielectric constant that diverges towards low frequencies. However, in various recent reports<sup>1,2,4-6</sup> giant values of the dielectric constant were claimed to persist over broad temperature ranges and, when plotted as a function of frequency, revealing an almost constant low-frequency value and a steplike decrease of the dielectric constant towards higher frequencies. This steplike decrease, which is accompanied by a loss peak in the imaginary part of the permittivity,  $\epsilon''$ , shifts exponentially to higher frequencies with increasing temperature, characteristic of Debye-like dipolar relaxation with a thermally activated relaxation rate. Several intrinsic physical interpretations have been given. Examples include almost incipient ferroelectricity in high- $T_c$  materials,<sup>2</sup> highly polarizable relaxation modes,<sup>5</sup> or a relaxorlike slowing down of dipolar fluctuations in nano-sized domains.<sup>6</sup> However, in Ref. 7 it was suspected that extrinsic effects may play a role in the CDC reported in Ref. 6.

In the present paper we provide evidence that many of these observations are not intrinsic in origin and we speculate that most, if not all, of the CDC's reported so far are based on Maxwell-Wagner-type extrinsic effects.<sup>8</sup> We will promote the notion that the most natural explanation of apparent CDC's is contact effects and that in ceramic samples grain boundary effects may play a similar role and further "enhance" the dielectric constant. At these interfaces (metal-to-insulator contacts, intergrain boundaries) depletion layers are formed yielding Maxwell-Wagner-type relaxations when

measured by standard dielectric techniques that use metallic electrodes and two-point contact configurations. Thus, while some of the reports may indeed be based on intrinsic effects, extrinsic effects have to be excluded by carefully studying the materials using different sample geometries and different contact configurations, and analyzing the results in terms of electronic networks as considered in detail decades ago.<sup>9,10</sup> In the present paper, we propose a simple network that is derived from the models outlined by the classical works of Jonscher,<sup>9</sup> and Macdonald,<sup>10</sup> and others. We show examples on a series of different materials, where we observed CDC's, all of which being due to contact effects. Most of the investigated samples are single crystals, but we also provide results on a ceramic sample to evidence effects of grain boundaries on the dielectric response.

The inset to Fig. 1(a) shows the equivalent circuit that describes the main features of the dielectric response of almost all doped or dirty semiconductors. The circuit consists of a leaky capacitor connected in series with the bulk sample. As indicated in the equivalent circuit, the intrinsic bulk response is given by the sum of dc conductivity ( $\sigma_{dc}$ ), frequency-dependent ac conductivity—for which we use the universal dielectric response (UDR) ansatz  $\sigma'_{ac} = \sigma_0 \omega^s$ ,  $s < 1$  (Refs. 9 and 11)—and the high-frequency dielectric constant  $\epsilon_\infty$ .<sup>12</sup> The UDR is the most common approach to take into account the hopping conductivity of localized charge carriers.<sup>13</sup> Under these assumptions, the intrinsic complex conductivity  $\sigma_{intrinsic}^* = \sigma'_i + i\sigma''_i$  is given by<sup>9,11</sup>

$$\sigma'_i = \sigma_{dc} + \sigma_0 \omega^s, \quad (1)$$

$$\sigma''_i = \tan\left(\frac{s\pi}{2}\right) \sigma_0 \omega^s + \omega \epsilon_0 \epsilon_\infty, \quad (2)$$

where  $\epsilon_0$  is the permittivity of free space. From the conductivity, the complex dielectric permittivity can be calculated by  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = i\sigma^*(\omega)/\omega\epsilon_0$ . This formalism does not assume any dipolar relaxation phenomenon in the compound under investigation. The leaky capacitor in the equivalent circuit of Fig. 1(a) represents the most common way to model contributions from the electrode-sample interface.<sup>9,10</sup> For semiconducting samples, these arise mainly

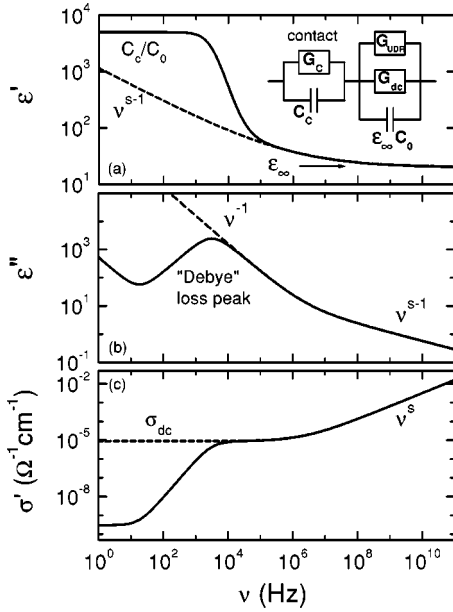


FIG. 1. Frequency-dependent dielectric response for the equivalent circuit shown in (a). Solid lines: overall response. Dashed lines: intrinsic bulk response as given by Eqs. (1) and (2). The circuit parameters have been chosen to reveal the prototypical behavior of doped semiconductors with Schottky-barrier-type contacts.

due to the formation of Schottky barriers in the region close to the metallic electrodes. If the electron work function in a metal is higher than in an electron semiconductor, then in the contact region of the semiconductor the electron concentration is suppressed, and a depletion layer appears. This relatively thin layer of small conductivity acts as a high capacitance in parallel with a large resistor, connected in series to the bulk sample. But also an accumulation of defects or deviations from stoichiometry (e.g., oxygen deficiency) near the sample surface may lead to such a capacitive surface layer.

In Fig. 1, the prototypical dielectric response that results from the equivalent circuit of Fig. 1(a) is shown. The solid lines represent the full dielectric response; the response of the intrinsic part alone is indicated by the dashed lines. At low frequencies,  $\sigma'(\omega)$  [Fig. 1(c)] exhibits a steplike increase, which can be ascribed to a successive bridging of the contact resistance (dominating the low-frequency response) by the contact capacitance acting like a short at high frequencies. The intrinsic contribution, following Eq. (1), is revealed only at high frequencies. Via the relation  $\varepsilon'' \sim \sigma'/\omega$ , the step in  $\sigma'(\omega)$  transfers into a peak in  $\varepsilon''(\omega)$  [Fig. 1(b)], thereby resembling the response of a Debye-like dipolar relaxation process. It is accompanied by a large steplike increase of  $\varepsilon'(\omega)$  towards low frequencies [Fig. 1(a)]. At low frequencies  $\varepsilon'(\omega)$  is dominated by the very high contact capacitance  $C_c$ , which when divided by the empty capacitance of the sample,  $C_0$ , leads to the apparently colossal values of  $\varepsilon' = C_c/C_0 > 10^3$ . Also for  $\varepsilon'(\omega)$ , the intrinsic response is detected only at sufficiently high frequencies. The time constant of the circuit is approximately  $\tau \sim RC_c$ , with  $R$  being the intrinsic sample resistance. Assuming that the contact capacitance is nearly constant, the temperature dependence

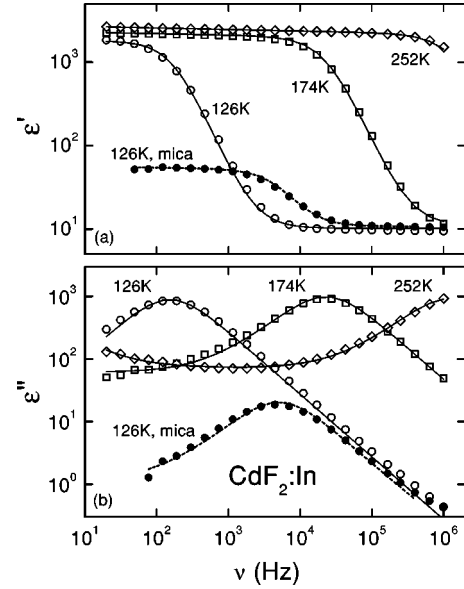


FIG. 2. Frequency-dependent dielectric response of single-crystalline  $\text{CdF}_2$  with sputtered gold contacts for three temperatures (open symbols) (Ref. 15). The solid circles show the results at 126 K for the same sample with a thin layer of mica between sample and electrodes. The lines are fits with the equivalent circuit shown in Fig. 1(a) including a distribution of contact parameters.

of the time constant is driven by the exponential increase of the charge carrier density of the semiconducting sample, leading to  $\tau \sim R_0 C_c \exp(E/T)$ , with  $E$  being a characteristic activation energy for charge carriers. Before demonstrating this type of response in a series of samples, we would like to state that in some cases the electronic equivalent circuit, shown in the inset to Fig. 1(a), is still too simple.<sup>12</sup> We have found that in more metallic samples the influence of inductance has to be taken into account at high frequencies, and sometimes the contacts are better represented using a distribution of time constants (several  $RC$  values). Furthermore, in ceramic samples other depletion layers can be formed at the interfaces of grain boundaries, yielding an additional step in  $\varepsilon'(\omega)$  and a further increase of the low-frequency dielectric constant. This will be demonstrated in one specific sample. However, we provide clear evidence that in most cases the simple equivalent circuit of Fig. 1(a) works rather well and accounts for the CDC's as well as for the relaxational behavior observed in many semiconducting dielectrics.

Our first example deals with measurements on single crystals of  $\text{CdF}_2$  doped with indium with contacts made from sputtered gold (for details, see Refs. 14 and 15). The experimental results and fits performed simultaneously for the real and imaginary parts with the simple equivalent circuit of Fig. 1(a) are shown in Fig. 2. Here  $\varepsilon'(\omega)$  [Fig. 2(a)] and  $\varepsilon''(\omega)$  [Fig. 2(b)] are shown in double-logarithmic representation.  $\varepsilon'(\omega)$  exhibits characteristic relaxation steps, reaching low-frequency values of about 2000, which are accompanied by well-pronounced loss peaks in  $\varepsilon''(\omega)$ . For the higher temperatures, at frequencies below the loss peaks,  $\varepsilon''(\omega)$  shows a minimum marking the transition to the

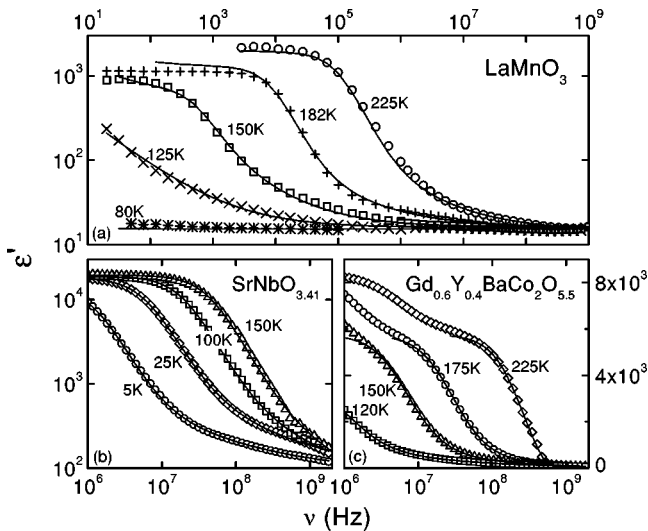


FIG. 3. Frequency-dependent dielectric constant of three transition-metal oxides for various temperatures. The lines are fits with the equivalent circuit shown in Fig. 1(a). (a) Single-crystalline  $\text{La}_2\text{MnO}_3$  (Ref. 16). (b) Single-crystalline  $\text{SrNbO}_{3.41}$  (Ref. 19). (c) Polycrystalline  $\text{Gd}_{0.6}\text{Y}_{0.4}\text{BaCo}_2\text{O}_{5.5}$  (Ref. 20). Here the fits were restricted to the high-frequency step, attributed to grain-boundary contributions (Ref. 20).

contact-dominated region. Compared to Fig. 1(b), this minimum is rather shallow, but using a distribution of contact barriers a very good agreement of fits and experimental data could be achieved. For the frequency and temperature range of Fig. 2, the UDR contribution can be neglected. In this specific semiconductor we carefully checked the influence of the contacts by measuring samples of different thickness and employing different contact electrodes. As an example, in Fig. 2 a second result obtained on the same sample ( $T = 126$  K), but with the electrodes separated from the bulk by a thin insulating layer of mica,<sup>14,15</sup> is given. Here no Schottky barriers are formed and the electrode capacitance is simply given by the mica layer. As shown by the dashed lines, the results can be fitted by the same equivalent circuit, leading to nearly identical bulk, but markedly different contact parameters. In both cases the intrinsic dielectric constant  $\epsilon_\infty \approx 10$  is far from being colossal or even unusually large. In order to exclude a Debye dipolar relaxation process, we also illuminated the sample by laser light.<sup>15</sup> It is obvious that the Debye relaxation time  $\tau_D$  should not depend on the light intensity. In our experiment the “relaxation frequency”  $\omega_p = 1/\tau = 1/(RC_c)$  was proportional to the light intensity due to an increase of the charge carrier density of the semiconducting sample.

Figure 3 shows  $\epsilon'(\omega)$  for three transition-metal oxides, all exhibiting apparently colossal dielectric constants at low frequencies. In Fig. 3(a), the dielectric response of  $\text{LaMnO}_3$ ,<sup>16</sup> the parent compound of all colossal magnetoresistance materials, is given. Pure  $\text{LaMnO}_3$  is an antiferromagnetic insulator. The finite carrier density probably results from a slight oxygen excess. The curves in Fig. 3(a) were taken at temperatures below the antiferromagnetic phase transition. Again we find the steplike decrease of  $\epsilon'$  on in-

creasing frequencies. The solid lines represent fits using our simple equivalent circuit. Here, the UDR had to be included in the fits, leading to a  $\omega^{s-1}$  contribution, which smears out the contact-dominated step in  $\epsilon'(\omega)$  at high frequencies. For the intrinsic dielectric constant we obtain  $\epsilon_\infty \approx 15$ . For doped manganates similar results were obtained, yielding somewhat higher, but certainly not colossal intrinsic dielectric constants.<sup>16,17</sup> We also want to refer the reader to our earlier work on single-crystalline  $\text{La}_2\text{CuO}_{4+\delta}$ , a parent compound of high- $T_c$  materials, which also reveals high nonintrinsic values of  $\epsilon'$ .<sup>18</sup>

Figure 3(b) shows the results for single-crystalline  $\text{SrNbO}_{3.41}$ , which is derived from the high- $T_c$  ferroelectric compound  $\text{SrNbO}_{3.5}$  and has been characterized as a one-dimensional metal.<sup>19</sup> In this case the intrinsic dielectric constant is rather high, reaching values of approximately 100. The low-frequency response approaches 20 000, simulating strong CDC behavior, which, however, arises only from the contacts.

Finally, in Fig. 3(c) we provide experimental evidence that in ceramic samples the response may be even more complicated. Figure 3(c) shows  $\epsilon'(\omega)$  for a perovskite-derived cobaltite,<sup>20</sup> revealing clear evidence for two successive steps. The high-frequency step, yielding values of  $\epsilon'$  close to 6000, is followed by a further increase towards low frequencies, which elevates  $\epsilon'$  to 8000 at MHz frequencies and  $T = 225$  K. While the low-frequency step is due to contact contributions, the second step can be attributed to grain boundary contributions, which yield a significantly different effective relaxation rate.<sup>20</sup>

In conclusion, using a variety of different compounds we demonstrated the occurrence of apparent “colossal dielectric constants” at audio and radio frequencies over a broad temperature range. By an in-depth analysis of the frequency- and temperature-dependent dielectric response, all these CDCs were revealed to result from contact or grain boundary effects. We believe that also most cases reported in the literature are of extrinsic origin. To pin down the ultimate origin and to exclude any extrinsic effects, different contact configurations and different sample geometries have to be utilized by the experimenters.

In what is left, we will consider the question if indeed a material with a nearly temperature-independent CDC could exist. For this purpose let us consider how nature can realize high dielectric constants and if those mechanisms could indeed lead to such a behavior. Two cases can be distinguished

(i) The first is that of permanent dipoles or the equivalent case of off-center ions within double-well potentials, often dominating the response in perovskite-related materials. It can lead to polar order at finite temperatures, relaxor ferroelectric behavior, or frozen-in disorder when the hindering barriers are too high. Such systems are well known and have been investigated in full depth. In all cases a strongly temperature-dependent dielectric constant of Curie or Curie-Weiss type will result. Obviously, permanent dipoles or off-center ions never can result in large dielectric constants that are temperature independent in a broad temperature range.

(ii) Thus it seems clear that only an electronic mechanism could be responsible for the occurrence of colossal,

temperature-independent dielectric constants. Again three cases can be distinguished: (a) Charge-density-wave (CDW) systems: the observation of very high dielectric constants in CDW systems, showing a relaxationlike behavior at audio- and radio-wave frequencies, is well established. In one of these systems a detailed analysis of the dielectric response has been performed by Cava *et al.*<sup>21</sup> using different types of contacts, thereby excluding contact contributions. This unusually large dielectric low-frequency response was later on explained theoretically by Littlewood to stem from pinned phason excitations.<sup>22</sup> (b) Materials close to a metal-to-insulator transition: diverging dielectric constants are also predicted for systems which are just at the borderline of a metal-to-insulator transition.<sup>23,24</sup> But we are only aware of one detailed experimental realization for doped silicon<sup>25</sup> yielding dielectric constants of  $10^3$ . (c) Electronic ferroelectricity: the occurrence of electronic ferroelectricity in correlated electron systems has been proposed in the framework of the Falicov-Kimball model.<sup>26</sup> It should occur in systems with a strong Coulomb interaction between localized and itinerant electrons in which the charge density breaks the

inversion symmetry of the underlying crystal lattice and results in electronic ferroelectricity. However, we do not know any realized example of such an electronic ferroelectric state. Excluding cases (a), (b), and (c), only the “normal” atomic polarizability remains to be considered: It is textbook knowledge<sup>27</sup> that the Clausius-Mosotti equation reveals a critical density where the dielectric constant diverges (this is valid for systems without permanent dipoles, which are considered here). However, this Clausius-Mosotti catastrophe occurs when  $(4\pi/3)\alpha$ , with  $\alpha$  the polarizability, reaches the particle volume itself, which, while not impossible,<sup>24</sup> seems unlikely at least.<sup>27</sup> Overall, only in CDW systems does a CDC behavior seem to be realized. If we leave out those systems, based on our experimental experience and on naive interpretations of the early work on dielectrics, we believe that the highest dielectric constants that can occur in condensed matter are of the order of  $10^2$ .

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<sup>12</sup>In principle, the minimal equivalent circuit configuration that is sufficient to qualitatively describe the characteristic Debye-like step in  $\epsilon'$  and the corresponding feature in  $\epsilon''$  or  $\sigma'$  includes only three elements: the sample conductance and capacitance and the contact capacitance. A very general equivalent circuit for a metal-insulator-semiconductor interface, including 14 ele-

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