The frequency-domain relaxation response of gallium doped $Cd_{1-x}Mn_xTe$

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Abstract
In this paper the complex dielectric permittivity of gallium doped Cd$_{0.99}$Mn$_{0.01}$Te mixed crystals is studied at different temperatures. We observe a two-power-law relaxation pattern with m and n, the low- and high-frequency power-law exponents respectively, satisfying the relation $m < 1 - n$. To interpret the empirical result we propose a correlated-cluster relaxation mechanism. This approach allows us to find origins of both power-law exponents, m and n.

1. Introduction

Gallium (Ga) doped Cd$_{1-x}$Mn$_x$Te is a group II–VI semiconductor, possessing deep metastable defects, called DX centers. The metastable character of the DX centers makes this mixed crystal a candidate for application in holography and high-density data storage [1]. It is fairly indisputable that the defects present in the material influence its properties [2, 3] and, at the same time, limit the parameters of devices based on them. Therefore, not only the development of experimental investigations but also that of theoretical studies is a crucial issue for gathering information concerning the properties of semiconductor mixed crystals with DX centers.

The DX centers are formed during the transition of Ga atoms from the substitutional position in the crystal lattice (shallow donor state) to the interstitial one (deep state). A passage from the shallow donor position to the DX state appears after the capturing of an electron by the dopant. Various charge states of the gallium dopant correspond to different placements of Ga atoms in the CdMnTe lattice. It has been found that the incomplete occupation of impurity states yields mutual correlation of the charge positions [4]. Consequently, positively and negatively charged impurities may form dipole-like objects. The presence of spatial correlations between the DX centers of different charge states was experimentally confirmed for HgSe:Fe, Hg$_{1-x}$Mn$_x$Se:Fe [5], GaAs [6], GaAs:Si [7], Al$_{1-x}$Ga$_x$As:Si [8] and CdTe:In [9]. Here, we present further evidence of the spatial correlations between the DX centers of different charge states. We analyze the dielectric spectroscopy data obtained for the gallium doped Cd$_{1-x}$Mn$_x$Te. We

argue that the frequency-domain relaxation response of this material, exhibiting low- and high-frequency fractional power laws, is characteristic for dipolar complex systems, i.e. the relaxation pattern is clearly of the non-Debye type. However, the main objective of this paper is to highlight the possible mechanisms underlying the observed relaxation properties of the material investigated. Our studies, based on the relaxation scenario of the correlated-cluster systems [10–12], explain the microscopic origins of the power-law exponents found experimentally.

2. Experiment

Gallium doped Cd$_{0.99}$Mn$_{0.01}$Te:Ga mixed crystals used in this study were processed by the Bridgman method. The room temperature net donor concentration, estimated from the capacitance–voltage (CV) characteristics, was found to be in the order of 10^{15} cm^{-3}. Gold Schottky contacts were thermally evaporated on the front side of the samples. The dielectric properties of the material were investigated using a Novocontrol impedance analyzer. The applied ac probe signal amplitude was equal to 10 mV. Measurements were performed at zero bias, in the frequency range from 0.2 Hz to 3 MHz, at temperatures in the range from 77 to 300 K.

3. Results and discussion

In figure 1 a sample complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ plot obtained for Cd$_{0.99}$Mn$_{0.01}$Te:Ga is presented in the Cole–Cole representation. It is known that for dipolar materials, relaxing in a manner similar to the classical Debye
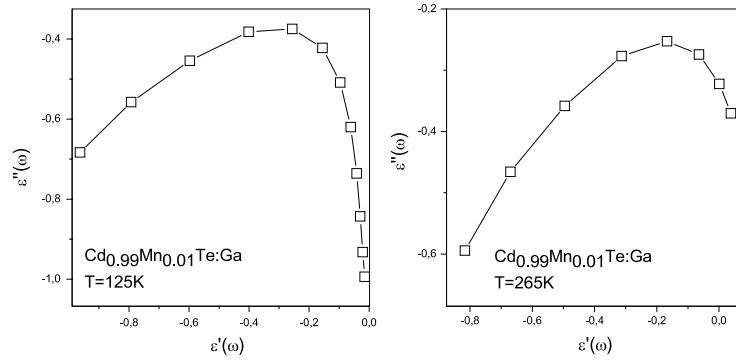
Figure 1. The complex permittivity diagrams (Cole–Cole plots) for two different temperatures. The asymmetric peak is a fingerprint of the non-Debye relaxation response of the sample investigated.
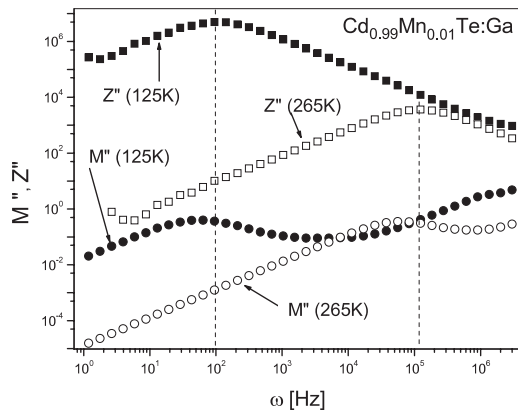

Figure 2. Double-logarithmic plots of the imaginary modulus M'' and impedance Z'' versus frequency, measured at two different temperatures.
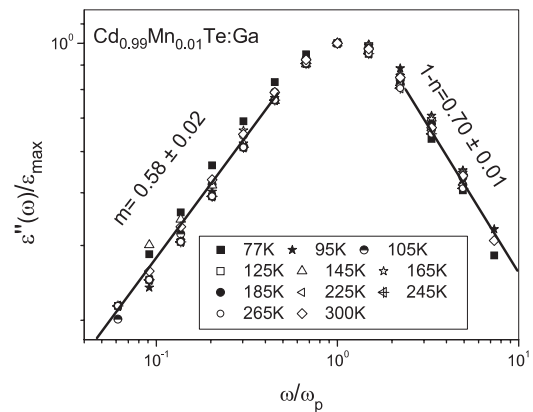

Figure 3. Double-logarithmic imaginary modulus and impedance versus frequency plots measured at different temperatures.

behavior, the $\varepsilon''(\omega)$ versus $\varepsilon'(\omega)$ plot approximates a semi-circle [13, 14]. However, for the material investigated the complex plane representation revealed an asymmetric, broadened peak implying a non-Debye relaxation pattern. The non-Debye relaxation of the sample was also confirmed by analysis of the dependence on frequency of the imaginary parts of the complex modulus $M^*(\omega)$ and impedance $Z^*(\omega)$, interrelated with the complex permittivity $\varepsilon^*(\omega)$ as follows:

$$\varepsilon^*(\omega) = 1/M^*(\omega),$$

$$M^*(\omega) = M'(\omega) + iM''(\omega) = i\omega C_0 Z^*(\omega),$$

where C_0 denotes the vacuum capacitance of the sample holder and electrode arrangement. It is represented by a shift of the maximum of the modulus $M''(\omega)$ and impedance $Z''(\omega)$ corresponding to the same temperature (cf figure 2). Moreover, regardless of the temperature, in both the $Z''(\omega)$ and $M''(\omega)$ curves single maximal peaks are detected. This observation indicates that the measured response is mainly influenced by the deep trap level located in the depletion region of the Au–Cd$_{0.99}$Mn$_{0.01}$Te:Ga Schottky junction investigated. Basically, the dominant trap in Cd$_{1-x}$Mn$_x$Te:Ga is the DX center associated with the gallium dopants [15]. Hence,

the relaxation response of this material is dominated by the metastable traps.

In figure 3 the normalized imaginary part of the complex permittivity $\varepsilon^*(\omega)$ is depicted. The normalization results in a master curve exhibiting also a single peak. Such a peak observed in the dielectric response of a sample is characteristic for dipolar systems [13, 14]. Indeed, this observation confirms the preliminary assumption of a dipole-like interaction between DX centers in different charge states. Dipolar properties of the system considered are not surprising at all. The relaxation behavior of the defects is studied experimentally, in response to a small oscillating voltage. At low frequencies (or high temperatures) the deep traps are expected to respond to the test signal, whereas at high frequencies (or low temperatures) the relaxation rates of the traps may be too small for this to happen. Besides, even within the same frequency or temperature regime there could appear traps which may not change their occupancy fast enough to contribute to the effective relaxation response. As a consequence, interaction between the deep defects responding instantaneously (emptied, positively charged centers—DX$^+$) and these which cannot emit carriers sufficiently fast (occupied, negatively charged centers—DX$^-$) is very probable. Moreover, it is clear from figure 3 that the dielectric response of Cd$_{0.99}$Mn$_{0.01}$Te:Ga follows the

anomalous relaxation mechanism [13, 14] represented by low- and high-frequency power-law dependence of the absorption term on frequency:

$$\varepsilon''(\omega) \sim (\omega/\omega_p)^m \qquad \text{for } \omega \to 0,$$
$$\varepsilon''(\omega) \sim (\omega/\omega_p)^{n-1} \qquad \text{for } \omega \to \infty, \tag{1}$$

where ω_p denotes the loss peak frequency and $0 < m$, $n < 1$. Similar two-power-law relaxation behavior (1) was observed by us in indium (In) doped $Cd_{1-x}Mn_xTe$; however, detailed analysis for this material will be a subject of another study. It should be pointed out that for the $Cd_{0.99}Mn_{0.01}Te$:Ga investigated, the fitting parameters satisfy the relation $m < 1 - n$ which cannot be interpreted by means of the well-known Havriliak–Negami function [13, 16] yielding the opposite inequality $m \geqslant 1 - n$. To interpret the physical significance of the experimental result for the gallium doped semiconductor mixed crystals we propose a stochastic mechanism which leads to a generalized Mittag-Leffler relaxation.

4. The relaxation model

Let us denote by N the number of the DX centers present in the system under consideration. Assume that some of the positively and negatively charged centers form dipole-like objects. The number K_N of dipoles formed is unknown (random). Assuming additionally that the ith dipole is surrounded by a random number N_i of single centers of the same charge, we note that K_N is equal to the largest number k such that $\sum_{i=1}^{k} (N_i + 1) \leqslant N$.

It is known that relaxations of the neighboring dipoles in a complex dipolar system may be correlated [12, 13]. The random number of the cooperating dipoles hence determines cooperative regions (superclusters) of sizes $M_1, M_2, \ldots$. The number L_N of randomly sized clusters (which itself is random) is equal to the largest l such that $\sum_{j=1}^{l} M_j \leqslant K_N$.

Following the most natural (historically oldest) approach to relaxation [13], the nonexponentiality of the relaxation behavior may be assigned to different local properties of the system investigated and interpreted in terms of a superposition of exponentially relaxing processes. The relaxation function $\Phi(t)$ is then assumed to take the form of a weighted average $\langle e^{-\tilde{\beta}t} \rangle$ with respect to the distribution of the effective (total) relaxation rate $\tilde{\beta}$:

$$\Phi(t) = \langle e^{-\tilde{\beta}t} \rangle = \int_0^\infty e^{-bt} g(b) \, db, \tag{2}$$

where $g(b)$ is the probability density function of the effective relaxation rate. The relaxation rate of the system as a whole is a sum of all L_N supercluster contributions. Similarly, the particular supercluster relaxation rate results from summing up the contributions of all dipole-like objects present in this cluster. Hence, the random total relaxation rate $\tilde{\beta}_N$ reads

$$\tilde{\beta}_N = \sum_{j=1}^{L_N} \sum_{i=1}^{M_j} \beta_{ijN}, \tag{3}$$

where β_{ijN} is the contribution of the ith dipole of the jth supercluster.

If the number N of DX centers in the material investigated is large (in practice it is enough when $N \sim 10^6$), one can replace $\tilde{\beta}_N$ with its limit in distribution $\tilde{\beta}$ as $N \to \infty$. The limiting random variable $\tilde{\beta}$, representing the effective behavior of the relaxing system, is well defined even with rather limited knowledge about the distributions of microscopic quantities: N_is, M_js, and β_{ijN}s. To apply the limit theorems for the sum (3) of the random relaxation rates we have to assume that: (i) $\beta_{ijN} = A_N^{-1}\beta_{ij}$ for some appropriately chosen constant $A_N > 0$ and a random variable β_{ij}, (ii) the sequences of random variables N_is, M_js, and β_{ij}s are stochastically independent, and (iii) each sequence consists of independent and identically distributed nonnegative random variables. If the random variables under considerations have heavy-tailed distributions with the tail exponents $0 < \lambda, \gamma, \alpha < 1$ and the scaling constants $\nu_0, \mu_0, b_0 > 0$, respectively[3], and $A_N = N^{1/\alpha}$, then the relaxation function (2) takes the following form:

$$\Phi(t) = \int_0^\infty e^{-bt/\tau_0} g_{\alpha,\lambda,\gamma}(b) \, db \tag{4}$$

with the characteristic material constant $\tau_0 = b_0^{-1}\left(\frac{\nu_0^\lambda \Gamma(1-\lambda)}{\Gamma(1-\alpha)}\right)^{1/\alpha}$, where $\Gamma(\cdot)$ denotes the gamma special function. The effective relaxation rate probability density function $g_{\alpha,\lambda,\gamma}(b)$ reads

$$g_{\alpha,\lambda,\gamma}(b) = \int_0^\infty \int_0^\infty x^{-1/\alpha} s_\alpha(x^{-1/\alpha}b) \frac{1}{\lambda} y^{1/\lambda} s_\lambda(y^{1/\lambda})$$
$$\times h_\gamma(xy) \, dx \, dy.$$

Here $s_a(x)$ is the probability density function of a completely asymmetric a-stable distribution such that $\int_0^\infty e^{-tx} s_a(x) \, dx = e^{-t^a}$ (for $a = \alpha$ or λ); and $h_\gamma(x) = (\Gamma(\gamma)\Gamma(1-\gamma))^{-1} x^{\gamma-1}(1-x)^{-\gamma}$ for $0 < x < 1$, and 0 otherwise, i.e. $h_\gamma(x)$ is the probability density function of a generalized arcsine distribution with parameter γ. Hence, the effective relaxation rate distribution $g_{\alpha,\lambda,\gamma}(b)$ is rather complex and can be interpreted as a mixture of the α-stable distribution $s_\alpha(x)$, the λ-trans-stable distribution $\frac{1}{\lambda}x^{1/\lambda}s_\lambda(x^{1/\lambda})$, and the γ-generalized arcsine distribution $h_\gamma(x)$.

Formula (4) can be rewritten into an equivalent, simpler form:

$$\Phi(t) = \int_0^\infty e^{-b(t/\tau_0)^\alpha} g_{\lambda,\gamma}^{(0)}(b) \, db \tag{5}$$

with

$$g_{\lambda,\gamma}^{(0)}(b) = \int_0^\infty \frac{1}{\lambda} x^{1/\lambda} s_\lambda(x^{1/\lambda}) h_\gamma(bx) \, dx$$

which is a mixture of the λ-trans-stable and the γ-generalized arcsine distributions only. For $\alpha = \lambda$ the relaxation function coincides with the generalized Mittag-Leffler relaxation function $\Phi_{GML}(t)$ with parameters λ, γ [17]. The type of relaxation response corresponding to this relaxation function

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3 The distribution of a nonnegative random variable, say X, has a heavy-tailed distribution if for large values of x the tail function $\Pr(X > x)$ exhibits a fractional power law $(x/x_0)^{-a}$ for some exponent $0 < a < 1$ and scaling constant $x_0 > 0$. The physical sense of the random variable X determines the dimension of the scaling constant x_0; hence ν_0 and μ_0 are dimensionless, while b_0 [s^{-1}].

was shown to exhibit two fractional power-law properties (1) with $n = 1 - \lambda$, $m = \lambda\gamma < 1 - n$. In the case of arbitrary $0 < \alpha < 1$, we have $\Phi(t) = \Phi_{GML}(t^{\alpha/\lambda})$. Hence, the time-domain response function $f(t) = -\frac{d\Phi(t)}{dt}$ reads as $f(t) = \frac{\alpha}{\lambda}t^{\alpha/\lambda-1}f_{GML}(t^{\alpha/\lambda})$. As a consequence, in the more general case also, the corresponding frequency-domain response $\varepsilon^*(\omega) \propto \int_0^\infty e^{-i\omega t} f(t)\, dt$ satisfies the two-power-law property (1) with the power-law exponents $n = 1 - \alpha$ and $m = \alpha\gamma < 1 - n$. Let us observe that the distribution of single centers N_i related to a particular dipole-like object does not influence the power-law exponents. Instead, it does influence the characteristic material constant. The low-frequency exponent m arises from the distribution of the cluster sizes (determined by the mutual correlation between dipoles formed in the system) and the distribution of their relaxation rates. The high-frequency exponent n is related to the distribution of the individual dipole relaxation rate only.

5. Conclusions

In this paper the dielectric permittivity of gallium doped $Cd_{0.99}Mn_{0.01}Te$ was analyzed. It was found that the frequency-domain relaxation response of the sample studied exhibits a two-power-law pattern with $m = \alpha\gamma$ and $n = 1 - \alpha$, the low-and high-frequency power-law exponents respectively, satisfying the relation $m < 1 - n$. A complete understanding of the relaxation mechanism, underlying this response, requires an explanation of the microscopic origins of the parameters α and γ, both falling in the range $(0, 1)$. As far as α is concerned, the progress in the understanding of this parameter was already made a few years ago (see [18] and the references therein). It has been shown that this parameter arises naturally from the microscopic anisotropy which gives rise to a hierarchy of relaxation rates (relaxation times) not all of which have the same probability of occurrence. As we have shown above, the parameter α has its origin in the heavy-tailed individual dipole relaxation rate distribution. This microscopic property indicates the scale invariance of the relaxation rates in the $Cd_{0.99}Mn_{0.01}Te$:Ga investigated (i.e., regardless of the scale at which one is looking at the relaxation rate distribution, the same proportion of smaller and larger contributions to the effective, macroscopic relaxation rate would be detected). As regards interpretation of the parameter γ, the analysis presented shows that it arises from the scale invariant clustered structure of the material, i.e., from the heavy-tailed distribution of the supercluster sizes. In other words, γ has its origin in long-range dipole–dipole interaction yielding the heavy-tailed distribution of the cooperative-region sizes. Summing up:

- For the first time we have derived the generalized Mittag-Leffler relaxation function starting from the correlated-cluster-system relaxation scenario. As we have shown, this function is able to reproduce relaxation patterns observed for $Cd_{0.99}Mn_{0.01}Te$:Ga, not interpretable by means of the well-known and commonly used Havriliak–Negami function.
- We have confirmed not only the existence of short-range defect–defect interactions, yielding dipole-like objects in

the material investigated, but also stated the presence of interactions among the (DX^--DX^+) dipoles, which was not previously reported.
- The proposed model, taking into account the local randomness resulting from the microscopic anisotropy as well as the dipole–dipole interaction, explains the experimentally observed relaxation pattern of the material analyzed. Hence, the cooperative dipole–dipole regions (superclusters), responsible for the low-frequency relaxation properties, may be expected in materials possessing DX centers.
- Searching for the origins of the power-law exponents we have brought to light the scale invariant spatio-temporal properties of the material studied. We have also shown that the distribution of the number of the DX centers, surrounding the dipole-like (DX^--DX^+) object, influences the characteristic material time constant only and is not related to the power-law exponents.

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