Two-level systems in nonstoichiometric fluorite phases

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A study of the microwave dielectric properties of solid solutions $(MF_2)_{1-x}(RF_3)_x$, where M = Ca, Sr, Ba; R = Lu, Y; and $3\times10^{-3}\leqslant x\leqslant 0.3$, reveals two-level systems. Such systems have not previously been seen for structures of the fluorite type. They indicate a change in the structure of the crystal lattice in these compounds.

The nonstoichiometric solid solutions of the fluorites of Ca, Sr, and Ba with trifluorides of the rare earths and yttrium[1], which have attracted interest in connection with the problem of superionic conductivity, have the cubic fluorite lattice over a broad range of compositions $(CaF_2)_{1-x}(YF_3)_x: 0\leqslant x\leqslant 0.4$. A superstructural ordering of the fluorite lattice has been observed[2] for compositions $x = 5/m$ (where m is an integer in the range $m = 13$–19) synthesized under special conditions. The primary structural element of the homologous series of superstructures is a Y_6F_{37} cluster, which is ideally suited for the fluorite lattice. The Y^{3+} ions occupy six nearest sites in the cation sublattice. The inner (for the Y_6 octahedron) cube of eight F^- ions changes to an F_{12} cubic octahedron, in whose cavity there is yet another noncentral F^- ion. There is reason to believe that clusters of the Y_6F_{37} type may dominate all fluorite phases with $x\geqslant 10^{-3}$ (Refs. 3 and 4). This conclusion seems to be implied by the discovery of two-level systems in these phases, which we are reporting here.

The existence of two-level systems, which are known for a broad variety of entities, is linked with a tunneling of ions between two equilibrium positions that differ only slightly in energy. In the simplified theory of Ref. 5 for two-level systems with a "spin" of 1/2, a constant state density, $n(E) = \text{const}$, is assumed[1)] for $0\leqslant E\leqslant E_M$. Each two-level system is characterized by an E-independent electric dipole moment $\vec{\mu}$ and a transition dipole moment $\vec{\mu}'$ in an electric field $\mathbf{e}$ of resonant frequency $\omega = E/\hbar$. The imaginary part ϵ'' of the dielectric constant ϵ, which is associated with the absorption of the field $\mathbf{e}$ by resonant two-level systems, is given by[5]

$$\epsilon''_{\text{res}} = (4\pi^2/27)(\epsilon_0' + 2)^2 n\mu'^2(1 + e^2/e_c^2)^{-1/2}\tanh(\hbar\omega/2kT), \tag{1}$$

where e_c^2 is the critical field, and $\epsilon_0'\approx 7$ (for[7] CaF_2). The relaxation term in ϵ stems from the modulation of E by an alternating electric field with a depth $\Delta E = (2/3)(\epsilon_0' + 2)\mathbf{e}\vec{\mu}$:

$$\epsilon_{\text{rel}} = \epsilon'_{\text{rel}} - i\epsilon''_{\text{rel}}$$
$$= (4\pi/27)(\epsilon_0' + 2)^2(kT)^{-1}n\mu^2\int_0^{E_M} dE\,\text{sech}^2(E/2kT)[1 + i\omega\tau_1(E, T)]^{-1}. \tag{2}$$

For the direct "spin"-lattice relaxation, which is the primary process at $T < 10$ K, the

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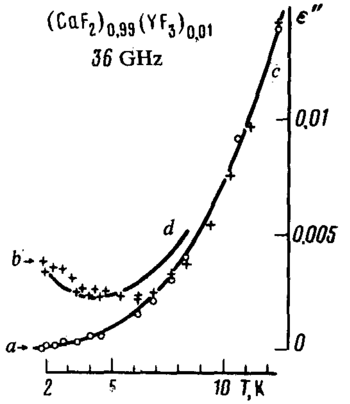

FIG. 1.

rate is $\tau_1^{-1}(E,T) = AE^3\coth(E/2kT)$, where A is a constant.[5]

In the present experiments, at $T = 1.8$–100 K, in the TE_{011} microwave resonators, we have $\omega/2\pi = 8.5$–9.5, 35–37, and 72–76 GHz for $(CaF_2)_{1-x}(RF_3)_x$ (R = Lu, Y and $3\times10^{-3}\leqslant x \leqslant 0.3$), $(SrF_{2\text{–}0.97}(LuF_3)_{0.03}$, and $(BaF_2)_{0.97}(LuF_3)_{0.03}$ samples. We study the dependence of $\uparrow\epsilon''$ on the microwave field in the resonator and on the temperature. We will discuss the results for the particular case of $(CaF_2)_{0.99}(YF_3)_{0.01}$, which demonstrate the existence of two-level systems in these samples.

Figure 1, a and b, shows the experimental curve of $\epsilon''(T)$ for two levels of the microwave power dissipated in the resonator, differing by 30 dB [the circles (a) represent the higher power]. We see that ϵ'' reaches saturation with increasing microwave field, so that the contribution of $\epsilon''_{\rm res}$ can be distinguished. At $T = 1.8$ K we find $e_c^2 = 10^{-2}$ esu (for $\omega/2\pi = 36$ GHz). Analyzing the time dependence of the relaxation to the steady-state value of $\epsilon''_{\rm res}(t)$ after the microwave field is applied for the same conditions, we find the estimate that τ_1 is a few times 10^{-7} s for two-level systems with $E = \hbar\omega$. As the microwave range is changed, we find $\epsilon''_{\rm res} \sim \omega$ with $e^2 \ll e_c^2$, in agreement with (1). For $T < 10$ K and $e^2 \ll e_c^2$ at which $\epsilon''_{\rm res}$ and $\epsilon''_{\rm rel}$ are comparable in magnitude, the experimental curve of $\epsilon''(T)$ agrees satisfactorily with the theoretical curve (Fig. 1, b and d). At the $\epsilon''_{\rm res}$ saturation with $e^2 \gg e_c^2$ (Fig. 1, a and c), we find $\epsilon'' \approx \epsilon''_{\rm rel} \sim T^3$, in agreement with (2) under the condition $\omega\tau_1(3kT) \gg 1$.

Over a broader temperature range at $T > 10$ K, with $\epsilon'' \approx \epsilon''_{\rm rel} \gg \epsilon'_{\rm res}$, the experimental curves of $\epsilon''(T)$ are as shown in Fig. 2a, but they can be described by a simple Debye law with a peak at $T = T_M$ (Fig. 2b):

$$\epsilon'' \sim \omega\tau_1(T)[1 + \{\omega\tau_1(T)\}^2]^{-1} = (T/T_M)^3[1 + (T/T_M)^6]^{-1},$$

where $T_M = 19$ and 30 K for $\omega/2\pi = 9$ and 36 GHz, respectively. [We will not discuss here the nature of the second peak in $\epsilon''(T)$ at ~ 80 K; Ref. 5.] On the other hand, theoretical expression (2) leads to a flatter maximum in $\epsilon''(T)$, even if Raman relaxation is taken into account,[6] since a broad spectrum, on the order of a few times kT, of "warm" two-level systems is involved in shaping the maximum.[5] The observed depen-

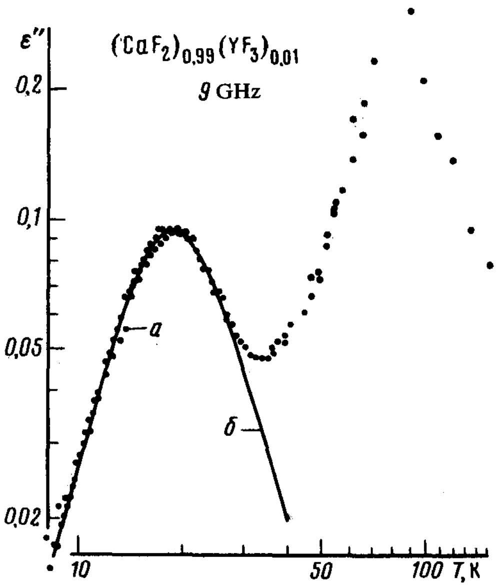

FIG. 2.

dence $\epsilon''(T)$ leads to the conclusion that the scatter in the relaxation times of the warm two-level systems at $T \sim T_M$ is considerably smaller in our case than follows from the rigorous theory of Ref. 6. This result may be evidence of the establishment at $T > 10$ K of a common relaxation time $\bar{\tau}_1(T) \sim T^3$, because of (for example), an effective cross relaxation which combines all the warm two-level systems into a common reservoir (after the example of electron spins[8]). Taking only the direct relaxation into account, we then have

$$\bar{\tau}_1^{-1}(T) = \int_0^{E_M} dE\,\mathrm{sech}^2(E/2kT)\tau_1^{-1}(E,T) \Big/ \int_0^{E_M} dE\,\mathrm{sech}^2(E/2kT) \approx 12.17A(kT)^3, \quad (3)$$

$$\epsilon_{\mathrm{rel}} = (8\pi/27)(\epsilon'_c + 2)^2 n\mu^2 [1 + i\omega\bar{\tau}_1(T)]^{-1}, \quad (4)$$

in agreement with the experimental data. At low temperatures, with $\omega\tau_1 \gg 1$, expressions (2) and (4) become the same.

We attribute the existence of two-level systems in the fluorite phases to a tunneling motion of the noncentral F^- ion in the Y_6F_{37} clusters. The establishment of a common $\bar{\tau}_1(T)$ is possible only if there is a large number of two-level systems per unit volume, and it is in complete agreement with the conclusion[3] that the samples studied contain "grains" of an R phase: a highly concentrated group of clusters, $\sim 10^{21}$ cm^{-3}. From experiment we have $E_M \geqslant 100$ cm^{-1}, $n\mu'^2 = 2 \times 10^{-4}$, and $n\mu^2 = 3 \times 10^{-3}$. From the lower estimate of E_M we find $n = 10^{33}$ erg$^{-1}\cdot$cm^{-3}, $\mu' = 0.4$ D, and $\mu = 1.7$ D, in agreement with the value $\mu = 2.2$ D which would be expected for our model on the basis of Ref. 2. Using the value of e_c^2 at $T = 1.8$ K, we can estimate the minimum width of the hole burnt by the microwave pump in the $n(E)$ distribution[5]: $\delta = (2/$

$27)(\epsilon_0' + 2)^2 \hbar^{-1} e_c^2 \mu'^2 \tau_1 = 0.02\ \text{cm}^{-1} \ll kT$. It follows that at $T = 1.8$ K a common $\bar{\tau}_1(T)$ is not established. Furthermore, such a small value of δ can be explained only by assuming a statistical distribution of warm two-level systems over the entire volume of the crystal, without the grouping into grains (i.e., the number of warm two-level centers in each grain is small at $T = 1.8$ K). We can thus estimate the size of these grains to be ~ 100 Å.

We will briefly summarize the other results. In the $(\text{CaF}_2)_{1-x}(\text{RF}_e)_x$ samples the low-temperature dielectric loss increases in proportion to x and is independent of R = Lu, Y. Quenching these samples from 950 °C causes a reduction of ϵ'' by a factor of ~ 5, while a subsequent annealing at 900 → 400 °C completely restores the value of ϵ'', in agreement with the behavior of clusters during such treatment.[7] In the solid solutions of SrF_2 and BaF_2, we again observe two-level systems, but at low temperatures ϵ'' is several times smaller (in the case of SrF_2) or an order of magnitude smaller (in the case of BaF_2) than in solid solutions of CaF_2 of otherwise the same composition. The differences may stem from the different probabilities for the capture of a pair of F^- ions into the cavity of the cubic octahedron (as discussed above), and thus a termination of the tunneling, for these solid solutions.[4]

On the basis of Refs. 2–4 and 7, we can now reliably predict the existence of two-level systems for solid solutions of fluorite with all the fluorides of the second half of the rare-earth series. The existence of two-level systems can explain [see expression (4) with $\omega \bar{\tau}_1(T) \ll 1$] the sharp increase ($\Delta\epsilon_0' = 50x$) observed[7] in the dielectric constant measured at low frequencies, ~ 1 kHz, in $(\text{CaF}_2)_{1-x}(\text{ErF}_3)_x$ samples with a very weak temperature dependence at $T > 5$ K. Our results also correlate with the decrease which has been observed[7] in the increment $\Delta\epsilon_0'/x$ in the series of bases CaF_2–SrF_2–BaF_2.

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1) See Ref. 6 for the application of a more rigorous theory of a double distribution of two-level systems.

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