pendently of the presence of a crystal field, unlike the situation for the electric field formalism, where the effective Hamiltonian idea fails without a sufficiently strong crystal field, is understandable on simple physical grounds, and suggests that the magnetic field formalism should, if anything, be better founded than the electric field formalism. Nevertheless, all our magnetic field results must be qualified, in this paper, as being true "to all powers in the field," and we have been unable, so far, to do anything for the magnetic field problem analogous to Sec. 3. The difficulty here is, perhaps, related to the greater richness of phenomena produced by a magnetic field in a solid, compared to the basic simplicity of most electric field effects. It would, however, be very desirable to be free of the power series limitation, since the recent work of Cohen and Falicov[9] on "magnetic breakdown" suggests that there might be specific difficulties with the band index $q$ as the field is varied, and the power series might only be an asymptotic representation of electron behavior.

### ACKNOWLEDGMENTS

We wish to express our thanks to Dr. E. Blount and Professor J. L. Powell for helpful discussions.

[9] M. H. Cohen and L. M. Falicov (unpublished).

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# Microwave Losses in Strontium Titanate above the Phase Transition*

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The microwave losses in both pure and doped $SrTiO_3$ have been investigated as a function of frequency and temperature. It is found that the loss tangent is proportional to frequency in the range 3–36 kMc/sec. Above the phase transition at 112°K, the temperature dependence of the loss tangent is well represented by $\tan\delta=(T-T_c)^{-1}(\alpha+\beta T+\gamma T^2)$, where the Curie temperature, $T_c=37$°K. The parameter $\alpha$ is shown to be determined by lattice imperfections and vanishes for pure single-crystalline material. The parameters $\beta$ and $\gamma$, which are related to third- and fourth-order anharmonic terms in the interionic potential, are shown to be intrinsic properties of the perfect lattice and are unaffected by imperfections.

## INTRODUCTION

MICROWAVE losses in ferroelectric materials have been the subject of many studies in the past years. Powles and Jackson[1] and others[2] have measured the losses of barium and strontium titanate mixtures as a function of temperature and composition. At 3 kMc/sec, Davis and Rubin[3] have investigated the loss tangent of certain mixtures of $Ba_xSr_{1-x}TiO_3$ above and below the Curie temperature. Work on single crystals of $BaTiO_3$ has been published by Benedict and Durand.[4] In all these cases the microwave losses were relatively high even above the Curie temperature, obviously the main reason why such attractive properties like the nonlinearity of the dielectric constant have not yet been utilized in such materials to any appreciable extent. Recently we have shown that the microwave losses in single crystalline strontium titanate are surprisingly low above the Curie temperature, and that $SrTiO_3$ is potentially a good substance to study the loss mechanism in dielectric materials.[5]

$SrTiO_3$ is commercially available in relatively high purity as single crystals.[6] In the low-frequency range at room temperature Linz[7] has reported a loss tangent of $2.5\times10^{-4}$ which is independent of frequency in the range between $10^2$ and $10^7$ cps.

It is the purpose of this paper to report in some detail on the functional dependence of the loss tangent at microwave frequency on parameters such as temperature, frequency, and lattice imperfections, and hereby strive for an answer to the question: Are the observed microwave losses intrinsically connected with the property of ferroelectricity and therefore unavoidable, or are they in part due to lattice imperfections and other disturbing factors? Many of the following experiments described below were carried out on single crystalline $SrTiO_3$. The data presented have been taken above the Curie temperature and will be evaluated in

* Work supported in part by the Electronics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, under contract, and by the U. S. Army Signal Research and Development Laboratory under contract.

[1] J. G. Powles and W. Jackson, Proc. Inst. Elec. Engrs. (London) **96**, 383 (1949).

[2] A. von Hippel, Revs. Modern Phys. **22**, 221 (1950); A. Lurio and E. Stern, J. Appl. Phys. **31**, 1805 (1960); Phys. Rev. **123**, 117 (1961).

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[4] T. S. Benedict and J. L. Durand, Phys. Rev. **109**, 1091 (1958).

[5] R. O. Bell and G. Rupprecht, Bull. Am. Phys. Soc. **6**, 12 (1961).

[6] The single-crystal $SrTiO_3$ was obtained from the National Lead Company.

[7] A. Linz, Phys. Rev. **91**, 753 (1953).

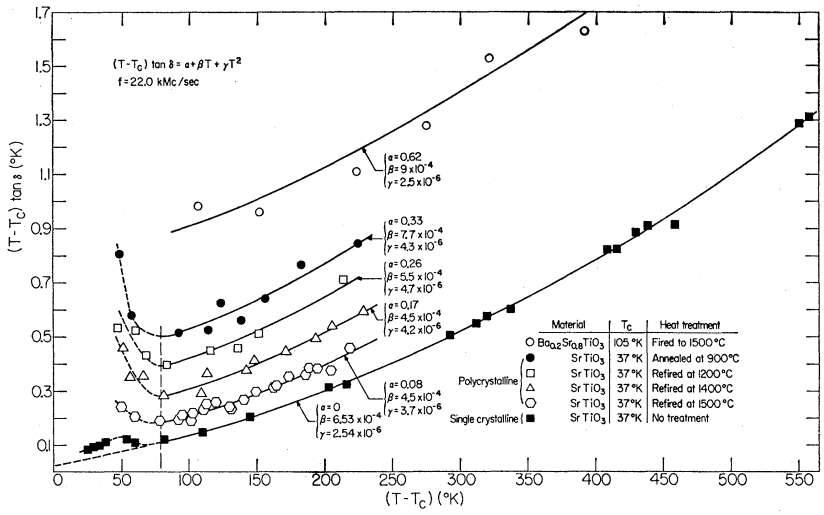


FIG. 1. $(T-T_c)\tan\delta$ vs $(T-T_c)$ for single-crystal $SrTiO_3$; for a polycrystalline $SrTiO_3$ sample successively refired to 900°, 1200°, 1400°, and 1500°C; and for polycrystalline $Ba_{0.2}Sr_{0.8}TiO_3$ at 22.0 kMc/sec.

this paper only above 112°K, the temperature $T_a$ at which a phase transition occurs in $SrTiO_3$. This phase transition has been deduced from paramagnetic resonance work by Müller[8] who quotes a transition temperature of about 100°K. Through studies on $Gd^{3+}$-doped $SrTiO_3$, Rimai[9] has determined a more precise value of $T_a=110$°K. This is in excellent agreement with the observations made by the authors of an abrupt change of the elastic properties at 112°K.[10]

In the course of this work the results on polycrystalline materials as well as annealing experiments became quite important for the interpretation of the data. Recently Silverman has worked out a theory of the microwave losses in ferroelectric materials in a simplified model.[11] The present experimental results will be compared with this theory and interpreted in terms of impurity scattering of the microwave photons and of third- and fourth-order anharmonic scattering.

## EXPERIMENTAL TECHNIQUE

To measure a relatively small loss tangent in the presence of a large and strongly temperature-dependent dielectric constant, as is the case for $SrTiO_3$, creates a problem of its own. The measurement was achieved by observing the $Q$ of a dielectric resonance in a piece of dielectric material with dimensions larger than the wavelength of the microwave field in the material. The sample was placed in a section of waveguide which was cooled by immersing in liquid nitrogen or heated by a resistance heater. The sample was allowed to warm up slowly, and the reflection from the sample was recorded as a function of temperature. As the sample warms, the dielectric constant changes and a series of reflections appear which correspond to various dielectric resonance modes. Since skin losses and radiation losses are negligible compared to the dielectric losses, the width of the resonance peaks is directly proportional to the loss tangent of the material.[12]

## MICROWAVE LOSSES IN POLYCRYSTALLINE CERAMIC MATERIALS

Polycrystalline $SrTiO_3$ was prepared by hot pressing. This process leads to a ceramic body of high density. The grain size, depending upon conditions during the sample preparation, is of the order of one micron. It has been observed that the samples are very lossy after hot pressing. It will be shown explicitly in subsequent annealing studies that this is to be attributed to a large number of lattice imperfections which are inherent to this type of sample preparation. The losses show roughly a Curie-Weiss behavior, that is, they are proportional to $(T-T_c)^{-1}$. This can be found implicitly in the data of other workers.[3,4]

One and the same sample was the subject of a series of annealing procedures in air for ten hours each. The annealing temperatures were 900°, 1200°, 1400°, and 1500°C. The loss tangent and the average grain size were measured after each annealing step. The losses at 22 kMc/sec are shown in four curves in Fig. 1. For experimental and theoretical reasons[11,13] the data are presented in the form $(T-T_c)\tan\delta$ vs $(T-T_c)$. $SrTiO_3$ is paraelectric in the investigated temperature range and its dielectric constant can be described quite well by a Curie-Weiss law[14]:

$$\epsilon=C/(T-T_c), \qquad (1)$$

where $C=8.25\times10^4$°K, $T_c=37$°K. $T_c$ is the extra-

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[9] L. Rimai, Bull. Am. Phys. Soc. **7**, 7 (1962).
[10] R. O. Bell and G. Rupprecht, Bull. Am. Phys. Soc. **7**, 7 (1962).
[11] B. D. Silverman, following paper [Phys. Rev. **125**, 1921 (1962)]. B. D. Silverman, Bull. Am. Phys. Soc. **6**, 12 (1961).
[12] R. O. Bell and G. Rupprecht, IRE Trans. **MTT-9**, 239 (1961).
[13] G. Rupprecht, R. O. Bell, and B. D. Silverman, Phys. Rev. **123**, 97 (1961).
[14] G. Rupprecht *et al.*, Air Force Cambridge Research Laboratory Final Report AFCRL-TR-60-37, Research Division, Raytheon Company, 1960 (unpublished).

TABLE I. The loss tangent of barium-strontium titanates for various heat treatments at 22.0 kMc/sec. $(T-T_c)\tan\delta=\alpha+\beta T+\gamma T^2$.

| | Sample | Heat treatment | Grain size ($\mu$) | Curie temperature (°K) | $\alpha$ (°K) | $\beta\times10^4$ | $\gamma\times10^6$ $(°K)^{-1}$ |
|---|---|---|---|---|---|---|---|
| Polycrystalline | $SrTiO_3$ | Hot pressed and fired in air at 900°C for 10 hr | 1 | 37 | 0.33 | 7.7 | 4.3 |
| | | Refired at 1200°C in air for 10 hr | 3 | 37 | 0.26 | 5.5 | 4.7 |
| | | Refired at 1400°C in air for 10 hr | 15 | 37 | 0.17 | 4.5 | 4.2 |
| | | Refired at 1500°C in $O_2$ for 6 hr | 30 | 37 | 0.08 | 4.5 | 3.7 |
| | $Ba_{0.2}Sr_{0.8}TiO_3$ | Hot pressed and fired in $O_2$ at 1500°C for 10 hr | 30 | 105 | 0.6 | 9 | 2.5 |
| | $Ba_{0.5}Sr_{0.5}TiO_3$ | Hot pressed and fired in $O_2$ at 1500°C for 10 hr | 30 | 218 | 2.0 | (9)[a] | (2.5) |
| | $Ba_{0.7}Sr_{0.3}TiO_3$ | Ceramic fired to 1375°C in air for 1 hr | 8 | 280 | 2.2 | (9) | (2.5) |
| | $Ba_{0.8}Sr_{0.2}TiO_3$ | Ceramic fired to 1300°C in air for 1 hr | 8 | 324 | 1.6 | (9) | (2.5) |
| Single crystal | $SrTiO_3$ | None | $\infty$ | 37 | 0 | 6.53 | 2.54 |
| | $SrTiO_3$+0.1% $Gd^{3+}$ | None | $\infty$ | 37 | 0.033 | (6.53) | (2.54) |
| | $SrTiO_3$+0.03% $Fe^{3+}$ | None | $\infty$ | 37 | 0.043 | (6.53) | (2.54) |

[a] Values in parentheses indicate that these values were assumed in order to determine $\alpha$.

polated Curie temperature. At first glance one can deduce from Fig. 1 that the loss is clearly decreasing with subsequent heat treatments. At the same time the average grain size (listed in Table I) increases from about 1 $\mu$ to roughly 30 $\mu$.

Grain growth is probably not the only effect of heat treatment. One may safely assume that each firing process also improves the perfection of the lattice within the grains. Both effects are included in the term "lattice imperfection." We shall attempt to assess the importance of these two contributions later.

In the temperature range above the transition temperature $T_a$ one can fit the data to the expression

$$(T-T_c)\tan\delta=\alpha+\beta T+\gamma T^2. \quad (2)$$

The parameters $\alpha$, $\beta$, and $\gamma$ have been obtained from best fits of the data to Eq. (2). The solid lines in Fig. 1 are calculated from the listed values for $\alpha$, $\beta$, and $\gamma$. The results are presented in Fig. 1 and Table I. For an annealing temperature of 1500°C, $\alpha$, $\beta$, and $\gamma$ can be obtained fairly accurately. The accuracy decreases, however, for the lower annealing temperatures where the data show more scatter. $\beta$ and $\gamma$ appear to vary somewhat from one annealing to the next. It is important to note that the values for $\alpha$ are fairly insensitive to the possible choice of $\beta$ and $\gamma$, and can be considered to be relatively accurate.

The substantial decrease of $\alpha$ with increasing annealing temperature strongly suggests that $\alpha$ represents the losses which are introduced by lattice imperfections. Another conclusion can be drawn tentatively from this experiment. Since $\beta$ and $\gamma$ remain essentially constant during the heat treatment, one may conclude that these parameters are characteristic of the microwave losses which are connected with the dielectric material itself and are therefore unavoidable. This feature will be substantiated in the following studies. Below 110°K the losses show a marked upturn. It will be assumed in the following discussion that this upturn is connected with the phase transition at $T_a$.[15] The experiment was carried out with one sample and was repeated with a second sample from the same material yielding almost the same results. For the 1500°C annealing the data were so close to each other that they are presented together in Fig. 1 without discrimination.

We shall now try to estimate roughly the relative importance of grain boundaries and lattice defects within the grains in producing $\alpha$. Let us assume that $\alpha$ is composed of two additive contributions $\alpha_I$ and $\alpha_G$ for imperfection and grain boundary scattering, respectively. One may further assume that the grain boundary contribution varies inversely with the grain boundary surface area per unit volume. If $D$ is the average grain size, then $\alpha_G$ is inversely proportional to $D$. We make now the further assumption that $\alpha_I$ is a monotonic function of the annealing temperature. This can be expected for a hot pressed sample since the perfection of the lattice within the grains will increase with increasing annealing temperature $T_i$. With these assumptions:

$$\alpha=\alpha_G+\alpha_I,\ \alpha_G\sim D^{-1},\ \alpha_I(T_i)>\alpha_I(T_{i+1})\ \text{for}\ T_i<T_{(i+1)};$$

we obtain an estimate for the grain boundary scattering:

$$\alpha_G\leq 0.1/D\ (°K),$$

where the average grain size $D$ is measured in microns. The results of this estimate are shown in Fig. 2. The same result is obtained with mixed polycrystalline ceramic materials as will be discussed in the next section.

[15] The evaluation of data below 110°K will not be included in this paper. The solid lines stop at $T_a$. The data below are connected by dashed lines.

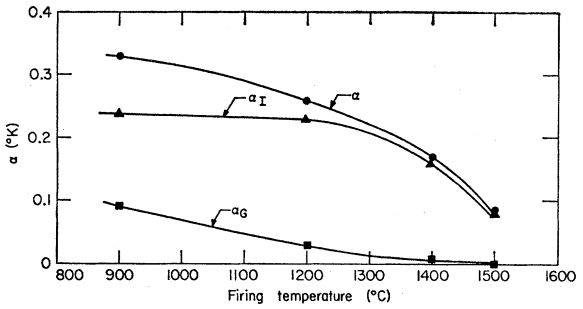


FIG. 2. $\alpha$ vs firing temperature for polycrystalline $SrTiO_3$. Also shown is $\alpha_G$ (contribution from grain boundary scattering) and $\alpha_I$ (contribution from imperfections) if it is assumed that $\alpha_I$ decreases monotonically with higher firing temperature.

## MICROWAVE LOSSES IN POLYCRYSTALLINE MIXTURES OF $Ba_xSr_{1-x}TiO_3$

In the previous experiment the importance of lattice perfection for the magnitude of the microwave losses and their connection with the impurity scattering constant $\alpha$ became apparent. It is of interest to find out how foreign ions will influence the losses in $SrTiO_3$. As an example, divalent barium may be substituted for divalent strontium in strontium titanate. $SrTiO_3$ and $BaTiO_3$ form a series of solid solutions. Lattice parameter and Curie temperature vary almost linearly with composition.[14] The samples were also prepared by hot pressing and fired at 1400°C. A refiring at 1500°C did not produce a noticeable change of the loss tangent as had been observed in polycrystalline $SrTiO_3$. The average grain size was about the same as in $SrTiO_3$ after the 1500°C annealing. The effect of grain boundaries is probably the same, as in polycrystalline $SrTiO_3$.

The result of loss measurements indicates that for a $Ba_{0.2}Sr_{0.8}TiO_3$ sample, $\alpha$ is appreciably in excess of the values for the $SrTiO_3$ specimen. It appears that the Ba content effects $\alpha$. It should be emphasized that $\beta$ and $\gamma$ come close to previous values. This is somewhat surprising since one might expect that in a substance with changed dielectric properties the anharmonic scattering terms might be different. It has been shown by the authors[13,14] that the nonlinearity constant $\langle A \rangle$, which characterizes the field dependence of the dielectric constant $\epsilon$, does not change appreciably with composition for mixtures of $(Ba,Sr)TiO_3$. Since the nonlinearity constant is closely related to higher-order anhamonic scattering, the consistency of $\beta$ and $\gamma$ becomes understandable. Again these data seem to support the statement that $\beta$ and $\gamma$ represent intrinsic properties of the lattice. The large value of $\alpha$ indicates that the introduction of barium into the $SrTiO_3$ lattice acts as an impurity. This is further demonstrated by a $Ba_{0.5}Sr_{0.5}TiO_3$ sample which has such a large loss tangent that the $\beta$ and $\gamma$ term could not be evaluated with sufficient accuracy. Therefore, the values of $\beta$ and $\gamma$, as determined for $Ba_{0.2}Sr_{0.8}TiO_3$, were used to determine $\alpha$ (Table I). A similar result was obtained with $Ba_{0.7}Sr_{0.3}TiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$. In Fig. 3, $\alpha$ is shown as a function of composition. As expected, a maximum of $\alpha$ appears between the two end members of this series of solid solutions.

The effect of grain boundaries on the loss tangent can be estimated from annealing experiments on mixed polycrystalline $Ba_{0.2}Sr_{0.8}TiO_3$ material. It was found that heat treatment which changed the average grain size by more than a factor of three decreased the loss tangent by less than 10%. A rough estimate shows an upper limit of the grain boundary contribution to be $\alpha<0.03$ for an average grain size of 15 $\mu$. The microwave losses were found to be proportional to $\omega$ and therefore to $\alpha$, $\beta$, and $\gamma$. In the mixed samples, where the major contribution to the loss originates from the impurity part, it is an explicit proof that at least $\alpha$ is proportional to $\omega$. The frequency dependence of $\beta$ and $\gamma$ has been obtained in detail from single crystals as will be noted later.

## MICROWAVE LOSSES IN SINGLE-CRYSTALLINE STRONTIUM TITANATE

The loss tangent of single-crystalline $SrTiO_3$ was measured in a temperature range from 60° to 600°K. The results for 22 kMc/sec are shown in Fig. 1. As was experienced with polycrystalline samples, one finds again an upturn of the loss tangent in the vicinity of the transition temperature $T_a$, suggesting that below the transition temperature the loss tangent shows a different behavior.

Above the transition temperature, however, the data are accurate enough to yield fairly good values for $\alpha$, $\beta$, and $\gamma$. In single-crystalline material $\alpha$ becomes zero, whereas $\beta$ and $\gamma$ are of the same order of magnitude as before. The data are listed in Fig. 1 and Table I.

Measurements at various frequencies between 3 and 36 kMc/sec have shown that within experimental error $\tan\delta$ is directly proportional to frequency. As a function of temperature the loss tangent exhibits the same general behavior, except that it is shifted proportional

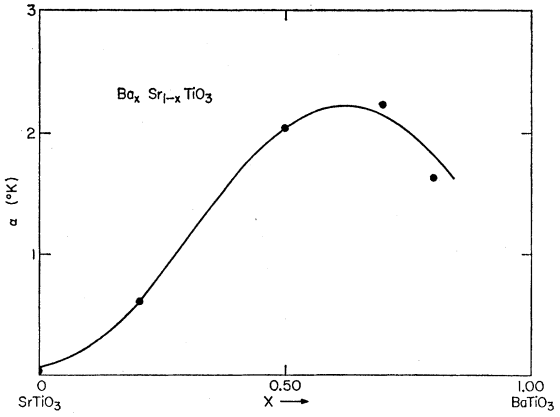


FIG. 3. $\alpha$ as a function of composition for $Ba_xSr_{1-x}TiO_3$ at 22.0 kMc/sec.

to the probing microwave frequency. Figure 4 shows tan$\delta$ vs frequency at 160°K. Since $\alpha=0$ for single crystalline material, one may conclude that $\beta$ and $\gamma$ are proportional to $\omega$.

## MICROWAVE LOSSES IN DOPED SINGLE CRYSTALS OF $SrTiO_3$

Attempts to influence the loss tangent by bombardment with 2-Mev electrons were unsuccessful. Annealing of single crystals at temperatures of 1500°C for up to 15 hr had no measurable effect on the loss tangent. The effect of oxygen vacancies in $SrTiO_3$ single crystals and doping with trivalent $Gd^{3+}$ and $Fe^{3+}$ ions, however, will be reported in more detail.

### Oxygen Vacancies

If strontium titanate is fired in a reducing atmosphere, the practically colorless crystal changes to a deep blue. The single crystal is now oxygen deficient and exhibits an $n$-type electrical conductivity. One might expect that the introduction of oxygen vacancies would disturb the crystal lattice and show an effect on the dielectric loss tangent. The electrical conductivity, of course, adds to the observed loss. This contribution, however, can easily be separated since the frequency dependence of the conduction losses is proportional to $\omega^{-1}$. Loss measurements as a function of temperature at various frequencies have been made on this material.

In the high-temperature region the losses can be accounted for by a real conductivity,

$$\sigma=\sigma_0 \exp(-\Delta E/kT), \tag{3}$$

with $\sigma_0\simeq 600$ mho/m and $\Delta E\approx 0.09$ ev. For the low-temperature region the losses are identical to those in an untreated single crystal. Furthermore, the dielectric constant does not deviate from that of normal single crystalline material. This experiment, therefore, shows the unexpected result that in the present concentration, oxygen vacancies do not change the dielectric loss tangent. The vacancy concentration may be estimated from $\sigma_0$ and a value for the mobility of the order of

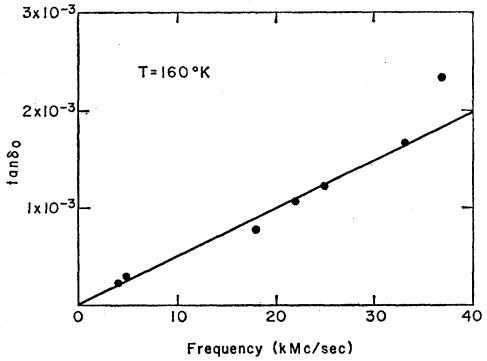


FIG. 4. Dielectric loss tangent of single-crystal $SrTiO_3$ as a function of frequency at 160°K.

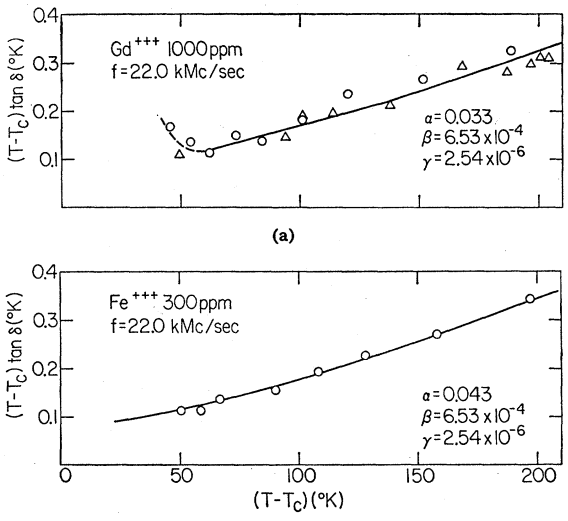


FIG. 5. $(T-T_c)$ tan$\delta$ vs $(T-T_c)$ for $SrTiO_3$ doped with (a) 0.1% gadolinium and (b) 0.03% iron.

$\mu\simeq 10$ cm²/v sec which has been obtained from weight-loss determination and conductivity measurements in heavily doped single crystals. This mobility value compares quite well with $\mu\approx 6$ cm²/v sec which has been found by Andrews and Weise[16] through Hall effect measurements on ceramic $SrTiO_3$ material. The concentration of vacancies amounts to roughly 0.03%. One might argue that such a relatively small number of lattice defects might not be enough to influence the loss tangent at any appreciable rate. It will be shown next that this concentration is sufficient to cause an increase of the impurity scattering when other doping agents are used.

## DOPING WITH $Fe^{3+}$ AND $Gd^{3+}$ IONS

Through paramagnetic resonance studies, Müller[8] has shown for iron and Rimai[9] for gadolinium, that these impurities are present as trivalent substitutional ions. The position of these impurities in the crystal lattice is somewhat uncertain. It is probable that $Gd^{3+}$ occupies a strontium site, whereas $Fe^{3+}$ occupies a titanium site. The iron and gadolinium concentrations were 0.03% and 0.1%, respectively. Figures 5(a) and 5(b) show the result of loss measurements. The experimental points were fitted as before by using Eq. (2). $\beta$ and $\gamma$ were taken as determined from single-crystal data. $\alpha$ is now no longer zero. The good fit as seen in Figs. 5(a) and 5(b) indicates that $\beta$ and $\gamma$ are material constants independent of the particular boule from which the sample is taken. It can be noted that gadolinium even though present in a larger concentration did not increase the losses as much as iron.

[16] E. K. Weise and M. C. Andrews, Office of Scientific Research OSR-Project No. 52-670A-85, Technical Note No. 11, 1958 (unpublished).

## DISCUSSION

The experimental data presented above can be summarized as follows:

a. $\tan\delta$ is proportional to $\omega$ for all specimens in the measured frequency range from 3 to 36 kMc/sec.

b. $(T-T_c)\tan\delta=\alpha+\beta T+\gamma T^2$ for all specimens in the temperature range from $T_a$ to 600°K, where $T_a$ is the temperature at which $SrTiO_3$ undergoes a phase transition.

c. In heavily doped and unannealed specimens the parameter $\alpha$ determines $\tan\delta$. In subsequent annealing of pure polycrystalline samples, $\alpha$ decreases monotonically and is negligible for pure single crystals.

d. The parameters $\beta$ and $\gamma$ are essentially independent of sample preparation and heat treatment.

We conclude therefore that $\beta$ and $\gamma$ are intrinsic properties of this nonlinear dielectric material. On the other hand, $\alpha$ is determined by lattice imperfections. In particular, grain boundaries contribute negligibly to $\alpha$, while impurities, even in a concentration of 0.03%, lead to a noticeable change in this parameter. It is clear on theoretical grounds that the loss cannot be due to absorption or emission of single phonons. Energy and momentum cannot be simultaneously conserved in the process, since the momentum of the microwave photon is negligible compared to the momentum of the excited phonon. It is possible, however, to excite a virtual phonon which subsequently decays into a real phonon due to interactions with lattice imperfections. The imperfection simply plays the role of absorbing the momentum of the phonon. Due to anharmonic interactions between the phonons, other decay processes are possible.[17] For example, third-order anharmonic interactions lead to the decay of a virtual phonon into two real phonons, or the virtual phonon may be destroyed by scattering a thermally excited phonon. Similar processes occur for fourth- and higher-order interactions.

In the subsequent paper[11] Silverman has worked out the temperature and frequency dependence of the loss tangent due to impurity and anharmonic damping. His results exhibit the same functional form as found in our experiments. In agreement with the experimental data he finds that $\alpha$ is determined by lattice imperfections while $\beta$ and $\gamma$ are characteristic of the perfect lattice arising from third- and fourth-order anharmonic interactions, respectively.

## ACKNOWLEDGMENTS

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[17] The authors are indebted to J. R. Schrieffer for having pointed out to them these two majors possibilities for the decay of microwave photons.