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Internal Friction in Rutile Containing Ni or Cr

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Rutile containing Ni gives an internal-friction peak centered near 50°C at 2 kHz characterized by an activation energy $E=15.3\pm2.4$ kcal/mole and a characteristic relaxation time $\tau_0=3\times10^{-15\pm1.7}$ sec; this peak occurs for tensile stress along [100] or [110]. A peak centered near 200°C with $E=21.4\pm2.1$ kcal/mole and $\tau_0=8\times10^{-15\pm1.0}$ sec occurs for stress along [100] but not for stress along [110]. Rutile containing Cr gives similar peaks characterized by $E=13.5\pm2.4$ kcal/mole and $\tau_0=2\times10^{-14\pm1.6}$ sec and by $E=22.2\pm1.5$ kcal/mole and $\tau_0=4\times10^{-15\pm0.9}$ sec. Light reduction in vacuum decreases the amplitude of the low-temperature peak and enhances the high-temperature peak in both cases. Heavy reduction of rutile containing Cr removes both peaks but they reappear upon subsequent reoxidation. The evidence suggests that the motion of interstitial cations is involved and that reduction causes the formation of a compound defect. A tentative interpretation is given in terms of unpaired Ni^{3+} interstitials for the low-temperature peak and of interstitial pairs composed of Ni^{3+}-Ti^{3+} for the high-temperature peak in Ni-doped specimens; the corresponding peaks in Cr-doped rutile are tentatively interpreted in terms of Ti^{4+} interstitials and of interstitial pairs consisting of Ti^{4+}-Ti^{3+}. It is possible to have two charge-compensating Cr^{3+} on adjacent substitutional sites and preserve the last two models.

I. INTRODUCTION

PREVIOUS internal-friction studies[1,2] of nominally pure rutile showed that light reduction in vacuum caused the appearance of an internal-friction peak which was observed for tensile stress along the [100] direction but was not observed for stress along [110] or [001]. This orientation dependence ruled out oxygen vacancies as the defect responsible and an interpretation in terms of interstitial titanium (whose occurrence was suggested by Hurlen[3]) was attempted. This interpretation requires an explanation of why no peak was observed for stress along [110] as would be expected for single interstitials from symmetry arguments. One might assume that the [110] peak was too small to be detected, but an approximate calculation suggests that the peak should be large enough for easy detection.[2] A model involving paired interstitials was proposed,[2] which can explain the observed orientation dependence in the temperature range studied, provided the jump frequency for a rotational motion of an interstitial pair about [001] is very much lower than for a rotational motion about [110]. This model appears fairly reasonable crystallographically and will be considered in more detail in the discussion.

Early spin-resonance work by Chester[4] suggested that vacuum reduction caused the occurrence of interstitial Ti^{3+}. Spectra for Ti^{3+} having a dependence on orientation of the magnetic field characteristic of the interstitial site suggested by Hurlen have subsequently been observed by Yamaka and Barnes.[5] This observation strengthens the association of the internal-friction peak in vacuum-reduced rutile with interstitial Ti^{3+} but does not assist in deciding whether the assumption of paired interstitials is correct.

It appeared possible to use rutile doped with Ni to check the previously mentioned calculation which indicated that for single interstitial cations stress along [110] should produce a peak of about the same size (i.e., three-fourths as large) as stress along [100]. Gerritsen and Sabisky[6] interpreted their spin-resonance results to indicte 80 parts per million (ppm) Ni^{2+} in interstitial sites, 5 ppm Ni^{3+} in interstitial sites, and 2 ppm Ni in unknown valence state in substitutional sites. It was hoped to see an internal-friction peak in Ni-doped rutile of about the same size for [100] and [110] stress and this has been observed. For contrast, measurements were also made on rutile doped with chromium; this system has been studied by spin resonance and it appears to be well established[5,7,8] that substitutional Cr^{3+} is produced. Reducing experiments on Ni- or Cr-doped rutile have also been carried out to test the possibility that pairing occurs between the defects associated with foreign cations and interstitial Ti^{3+} introduced by reduction.

II. SPECIMENS

All specimens were synthetic single crystals grown by the Verneuil flame-fusion technique using an oxygen-hydrogen flame and using a seed crystal to control orientation. The TiO_2 powder was obtained from the National Lead Company; the analysis has been given.[9]

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TABLE I. Results calculated from internal-friction peaks.

Specimen (No., orientation, mole ppm dopant)	Condition[a]	Temp. range[b] (°C)	Frequency at peak Fundamental (Hz)	Frequency at peak overtone (Hz)	A (TQ^{-1} at peak) (°K)	E_{shape}[c] (kcal/mole)	E_{shift}[c] (kcal/mole)	t_0[c] (sec)
56,[110] 500 NiO	I	low	1492	4068	0.10	16.4±2.4(6)	15.2±4.1(3)	$8\times10^{-16\pm1.7}$(6)
		high				no peak detected		
64, [110] 1000 NiO	I	low	3278	8992	0.13	15.4 (2)		3×10^{-15} (2)
		high				no peak detected		
57, [100] 500 NiO	I	low	1383	3651	0.13	16.3±2.7(13)	14.9±1.5(4)	$1\times10^{-15\pm1.9}$(13)
		high	1383	3652	0.14	19.6±2.1(6)		$5\times10^{-14\pm1.0}$(6)
55, [100] 1000 NiO	I	low	1364	3496	0.27	14.3±1.4(9)	13.5±0.5(4)	$2\times10^{-14\pm0.9}$(9)
		high	1364	3497	0.17	21.9±1.1(5)	20.9 (2)	$4\times10^{-15\pm0.6}$(5)
	II	low				no peak detected		
		high	1365	3497	0.36	22.5±2.9(4)	21.8 (2)	$2\times10^{-15\pm1.3}$(4)
	IIa	low				no peak detected		
		high	1302	3506	0.26	22.2 (2)	24.3 (1)	3×10^{-15} (2)
53, [001] 1000 NiO	I	low				no peak detected		
		high				no peak detected		
63, [110] 50 Cr_2O_3	I	low	4904	···	0.08	16.9 (1)		1×10^{-15} (1)
		high				no peak detected		
62, [110] 100Cr_2O_3	I	low	1242	3397	0.13	16.0±2.1(4)	12.5 (2)	$1\times10^{-15\pm1.5}$(4)
		high				no peak detected		
60, [100] 250 Cr_2O_3	I	low	1250	3430	0.41	14.7±2.3(4)	12.3 (1)	$1\times10^{-14\pm1.6}$(4)
		high				no peak detected		
	III	low				no peak detected		
		high				no peak detected		
	IV	low	1252	3432	0.25	13.9±2.3(4)	10.2 (2)	$5\times10^{-14\pm1.6}$(4)
		high	1252	3431	0.50	21.4 (2)	22.7 (1)	1×10^{-14} (2)
	V	low	1252	3432	0.38	12.4±1.7(4)	11.0 (2)	$8\times10^{-13\pm1.1}$(4)
		high	1252	3431	0.38	22.2±2.2(6)	22.9±0.8(3)	$5\times10^{-15\pm1.1}$(6)
61, [001] 100 Cr_2O_3	I	low				no peak detected		
		high				no peak detected		

[a] I indicates 24 h at 900°C in 1 atm O_2. II indicates specimen reduced from condition I by 72 h at 800°C in vacuum (7×10^{-7} mm Hg). IIa indicates specimen reground from condition II. III indicates specimen reduced from condition I by 8 h at 1350°C in vacuum (2×10^{-3} mm Hg, some oil in system). IV indicates specimen partially reoxidized from condition III by 24 h at 1200°C in air. V indicates specimen further reoxidized from condition IV by 24 h at 900°C in 1 atm O_2.

[b] Low range from about 20°C to 120°C, high range from about 120°C to 250°C.

[c] Average value and standard deviation based on number of determinations in parentheses.

Powder mixtures were made using either NiO or Cr_2O_3 to achieve the composition of the starting powder given in column 1 of Table I. Crystals were grown in the form of rods up to 6 in. long with somewhat irregular cross sections; these were ground using a diamond wheel to produce cross sections of about 0.25 by 0.25 in. although no attempt was made to keep the dimensions constant from one specimen to the next. Crystals were grown with the rod axis parallel to [001], [100], or [110]. The reason for this choice of directions has been discussed.[2] Briefly, the [001] direction is useful for a reference specimen because stress along this direction should not cause an internal-friction peak for any point defect which is limited to jumps between initially equivalent sites. Stress along [100] should give a peak for either single interstitials or interstitial pairs of the type previously discussed[2]; stress along [110] should give a peak for single interstitials but not for interstitial pairs in the temperature range studied if the jump rate for rotation of pairs around [001] is very much less than for a rocking motion about [110].[2]

III. EXPERIMENTAL PROCEDURE

The variation of internal friction with temperature was determined by Forster's method in which a bar is suspended horizontally from two fiber-glass threads tied between the nodes for the fundamental and first overtone of flexural vibration. One thread was driven by a magnetic record-cutting head and the other was attached to a piezoelectric pickup. The driving frequency was varied until resonance occurred. The drive was then shut off and the resulting damped oscillation was recorded on a storage oscilloscope. The internal-friction value was then calculated from the time for the amplitude to decay to one-half its original value. Measurements were made in vacuum of about 50μ of Hg and the background value of Q^{-1} was as low as 2 or 3×10^{-5} for a carefully hung [001] specimen.

IV. RESULTS

Some of the curves of internal friction as a function of temperature are shown for Ni-doped specimens in Figs. 1 and 2 and for Cr-doped specimens in Figs. 3 and 4.

Each of the internal-friction peaks was fitted to the function

$$TQ^{-1}=A\ \mathrm{sech}(S+E/R_0T)+C,$$

where E is the activation energy, R_0 is the gas constant, $S=\ln\omega\tau_0$, T is the absolute temperature, ω is the angular frequency, A is an amplitude factor, and C is a constant to represent background. An equation of this type results from any model with a single relaxation time given by $\tau=\tau_0\exp(E/R_0T)$; see the treatment for an 8-position model, for example that found in Ref. 10. The curve fitting was done by expanding the sech into a Taylor series about trial values of E and S; the least-squares best estimates of corrections ΔE and ΔS were found using an orthonormalizing routine.[11] This process was repeated to converge on final values of E and S. The theoretical function gives a satisfactory representation of the data as Fig. 5 shows. The peaks were retraced on different days; the average values of E are listed as E_{shape} in Table I, together with a standard deviation whenever there were three or more determinations. The best estimate of τ_0 was calculated from the average S value and is given in Table I. An independent determination of the activation energy,

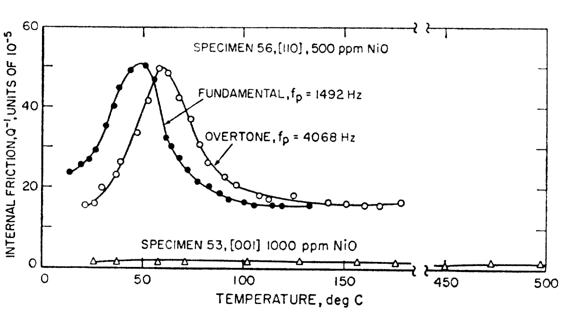

FIG. 1. Internal friction as a function of temperature for rutile containing Ni.

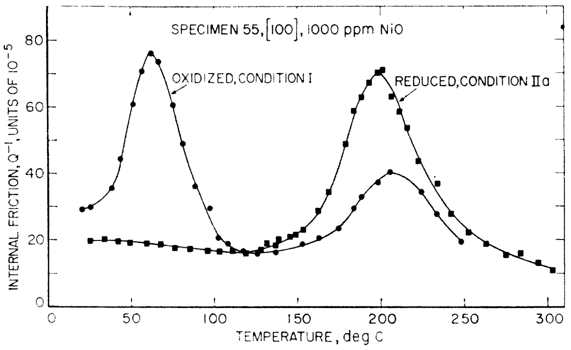

FIG. 2. Internal friction as a function of temperature for rutile containing Ni.

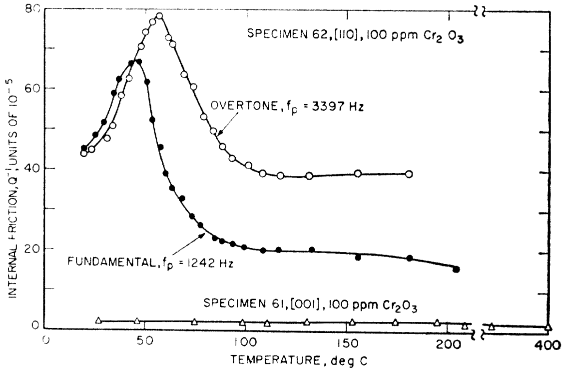

FIG. 3. Internal friction as a function of temperature for rutile containing Cr.

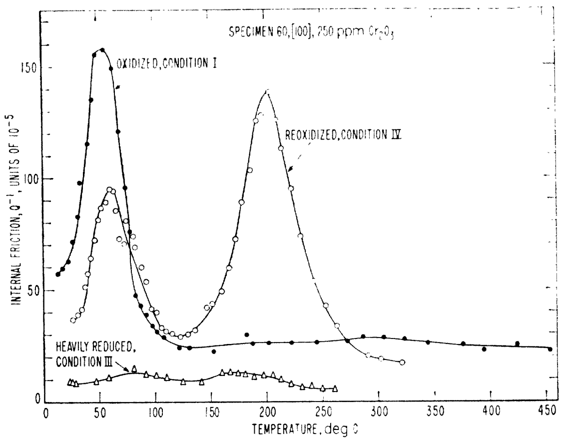

FIG. 4. Internal friction as a function of temperature for rutile containing Cr.

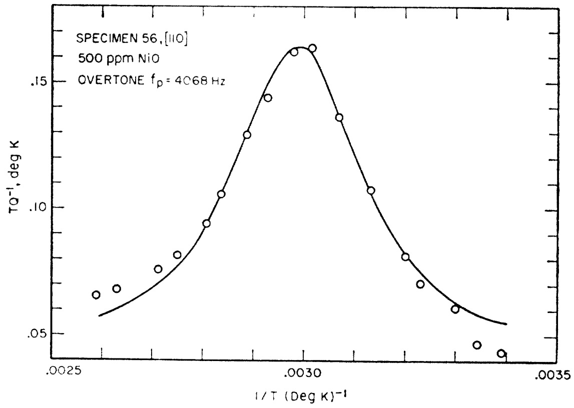

FIG. 5. Plot of theoretical function with parameters chosen to give best fit to experimental data.

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[11] P. J. Walsh, Commun. Assoc. Computing Machinery 5, 511 (1962).

TABLE II. Average values of E and τ_0 for four internal-friction peaks.

Dopant, temp. range	E_{shape}[a]	E_{shift}[a]	E[a]	τ_0[a]
Ni, low	$15.7 \pm 2.4(30)$	$14.4 \pm 2.1(11)$	$15.3 \pm 2.4(41)$	$3 \times 10^{-15 \pm 1.7}(30)$
Ni, high	$21.3 \pm 2.2(17)$	$21.9 \pm 2.5(5)$	$21.4 \pm 2.1(22)$	$8 \times 10^{-15 \pm 1.0}(17)$
Cr, low	$14.4 \pm 2.3(17)$	$11.2 \pm 1.1(6)$	$13.5 \pm 2.4(23)$	$2 \times 10^{-14 \pm 1.6}(17)$
Cr, high	$22.0 \pm 1.8(8)$	$22.8 \pm 0.7(4)$	$22.2 \pm 1.5(12)$	$4 \times 10^{-15 \pm 0.9}(8)$

[a] Average value and standard deviation based on number of determinations in parentheses.

listed as E_{shift} in Table I, was calculated from

$$E = T_1 T_2 R_0 (\ln \omega_2/\omega_1)/(T_2 - T_1),$$

where ω_1 and ω_2 are the frequencies of the fundamental and first overtone at the temperatures T_1 and T_2 at which the respective curves of TQ^{-1} peak.

Inspection of the values for E_{shape}, E_{shift}, and $\ln \omega \tau_0$ showed that the values for all peaks could be grouped together into four sets depending on whether they refer to the high- or low-temperature peak and whether the specimen was doped with Ni or Cr. The resulting averages given in Table II show that E_{shape} is equal to E_{shift} within experimental error so that each of the peaks is well described by a single relaxation time. The E_{shape} and E_{shift} values have therefore been averaged (giving them weights equal to the number of determinations of each) to arrive at a final best estimate of the activation energy listed as E in Table II.

The low-temperature peak occurs for stress along [100] or [110] in Ni-doped specimens in the initial condition (i.e., grown and subsequently heated to 900°C for 24 h in 1 atm O_2). Subsequent reduction of the [100] specimen caused the low-temperature peak to vanish and increased the size of the high-temperature peak. Subsequent reoxidation caused the low-temperature peak to reappear. These results (except for the reoxidation) are summarized in Table I and shown in Figs. 1 and 2. It is noteworthy that regrinding the specimen (Table I, conditions II and IIa) changed the size of the high-temperature peak; this result suggests uneven distribution of Ni.

In rutile doped with Cr a low-temperature peak occurs for both [100] and [110] stress and a high-temperature peak is seen for [100] stress although the latter peak was not seen in the initial condition. Heavy reduction produced a specimen having no internal-friction peak in the range of temperature investigated and subsequent reoxidation caused both peaks to appear. Further reoxidation increased the low-temperature peak and decreased the high-temperature peak.

V. DISCUSSION

Our discussion of the observed internal-friction peaks is based upon the following considerations:

(1) None of the peaks were found under [001] stress. This suggests that for each of the peaks observed under other stresses the defect responsible jumps between sites which are energetically equivalent in an unstressed crystal rather than between sites which are initially different in energy.

(2) The low-temperature peaks occur under [100] or [110] stress. For either Ni- or Cr-doped crystals the activation energy under [100] stress is the same, within experimental error, as that under [110] stress. An interstitial occupying a site of type *c* and jumping parallel to [001] would meet these requirements of the low-temperature peaks.

(3) The appearance of a high-temperature peak in either Ni- or Cr-doped crystals upon reduction is accompanied by a decrease in the corresponding low-temperature peak. This suggests that the defect responsible for the high-temperature peak is a compound one made up of combining the defect responsible for the low-temperature peak with the defect introduced by reduction.

(4) Any point defect in rutile giving a peak under [100] stress should also give a peak under [110] stress as shown by Table II of Ref. 2 or by the elastic-dipole treatment of anelasticity.[12] The observation of a high-temperature peak under [100] stress but not under [110] might result either if the peak in the [110] direction was too small to be detected or if the peak temperature for the [110] peak was different from that for the [100] peak and lay outside the temperature range of observation. A model of the latter type was suggested[2] for the peak observed around 120°C in nominally pure vacuum-reduced rutile; this model is a pair of interstitials lying at $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},\frac{1}{2})$ or equivalent pairs of positions. Jumping of both interstitials parallel to [001] but in opposite directions produces a rocking motion appropriate to the energy equivalence produced by [100] stress but not connecting arrangements made inequivalent by stress along [110]. Relaxation under [110] stress requires a jump perpendicular to [001] as shown in Fig. 6.

Models consistent with the observed peaks are shown in Fig. 7. For the Ni-doped specimens we suggest as the

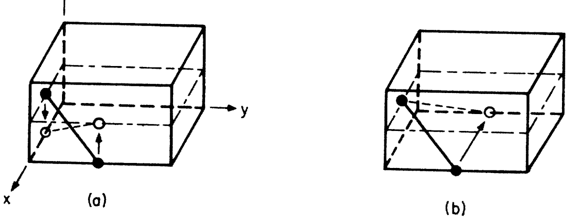

FIG. 6. The interstitial pair in rutile using the coordinate system of Fig. 1, Ref. 2. A rearrangement driven by [100] stress is shown in (a); one driven by [110] stress is shown in (b). Note that the former can occur entirely by jumps within channels parallel to [001] but that the latter or its equivalent requires at least one jump from one channel into another.

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cause of the low-temperature peak the 5-ppm interstitial Ni^{3+} per 87-ppm total Ni observed by Gerritsen and Sabisky. Interstitial Ti^{3+} introduced by reduction may form the pair shown in Fig. 7(b), which can account for the behavior of the high-temperature peak under [100] and [110] stresses provided the activation energy for the jump of Fig. 6(b) places the corresponding internal-friction peak outside the range of temperature used in the present work. The very large anisotropy for the diffusion of Li in rutile[13] lends some support to this idea. It is also necessary to assume that interchange of Ni^{3+} and Ti^{3+} does not cause a significant change of energy in order to account for the absence of peak under [001] stress as pointed out by Huntington.[14] The low-temperature peak in Cr-doped rutile is tentatively assigned to the motion of Ti^{4+} assumed as charge compensation for Cr^{3+} which is substitutional.[5,7,8] Ti^{4+} is assumed rather than Ti^{3+} because Cr-doped rutile is a good insulator and because no Ti^{3+} spectrum is observed in ESR experiments unless the specimen is reduced.[15] The high-temperature peak is tentatively assigned to the Ti^{4+}-Ti^{3+} pair of Fig. 7(c); the same assumptions must be made regarding this pair as for the Ni^{3+}-Ti^{3+} pair. The drawings of Figs. 7(e) and 7(f) show one way in which pairs of substitutional Cr^{3+} can be arranged and still permit the model to function because both positions of either defect are equally affected. The model of Fig. 7(f) has the further advantage that the two assumptions, mentioned above, which must be made for the pairs of Figs. 7(b) and 7(d) are no longer necessary. Similarly, for the Ni-doped rutile, the substitutional Ni in unknown valence state may be charge compensated by interstitial Ti^{4+} and the models of Figs. 7(e) and 7(f) may apply with Ni in place of Cr.

These models are complex, but all of the simpler models so far examined by the authors seem unsatisfactory. The type of argument previously presented[2] casts doubt on any simple unpaired substitutional or interstitial ion as the cause of the high-temperature peak.

It was previously found[1,2] that nominally pure reduced rutile showed a peak under [100] stress at about 120°C for frequencies around 2 kHz. The activation energy was the same, within experimental error, as that for the high-temperature peaks reported here. The 80°C lower temperature is caused by a very large frequency factor for the peak occurring in pure rutile.[2] The 120°C peak is not found in Ni- or Cr-doped rutile; this result is consistent with the models presented for the three peaks if one assumes that pairs of the type shown in Fig. 7 have higher binding energy than pairs of Ti^{3+} interstitials. One might suppose that upon further reduction all of the defects introduced by Cr or Ni would be paired with interstitial Ti^{3+} and that Ti^{3+}-Ti^{3+} pairs might then form and give a peak at 120°C. Highly reduced Cr-doped rutile gives no peak, however, suggesting that instead the pairs of Fig. 7 grow into clusters.

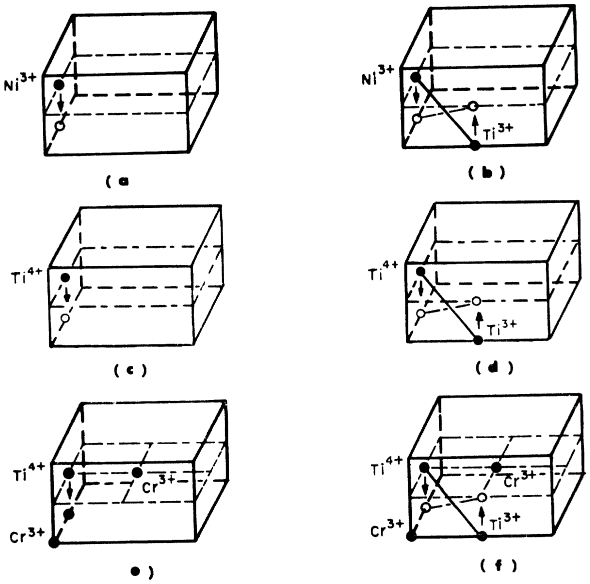

FIG. 7. Models consistent with the observed-interval friction peaks. Only deviations from the normal rutile structure are shown. Models consistent with the low- and high-temperature peaks in Ni-doped rutile are shown in (a) and (b), respectively; the simplest corresponding models for Cr-doped rutile are shown in (c) and (d). The possibility of adding pairs of substitutional Cr^{3+} to the latter is illustrated in (e) and (f).

Huntington and Sullivan[16] have proposed an explanation of the 120°C peak previously reported[1,2] in reduced, nominally pure rutile in terms of a pair consisting of a substitutional metal impurity paired with interstitial Ti^{3+} in a *d*-type interstitial site in the notation of the *International Tables for X-ray Crystallography*.[17] Nowick[18] has suggested a similar model using an interstitial site of type *c* rather than *d*. The present work indicates that the metal impurity must be something other than Cr or Ni.

Reliable interpretation of the internal-friction peaks associated with point defects in rutile presents a challenge. The model of Fig. 7(e) should give a dielectric-loss peak, but attempts to observe this peak have been inconclusive because of high background loss and high dielectric constant which are both frequency- and temperature-dependent. The models suggest the desirability of searching for an additional peak at higher

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[13] O. W. Johnson, Phys. Rev. **136**, A284 (1964).
[14] H. B. Huntington (private communication).
[15] E. Yamaka (private communication).
[16] H. B. Huntington and G. A. Sullivan, Phys. Rev. Letters **14**, 177 (1965); **14**, 932 (1965).
[17] *International Tables for X-ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch Press, Birmingham, England, 1952), Vol. I.
[18] A. S. Nowick (private communication).

and lower temperatures under [110] stress and of examining the dependence of peak height upon controlled and well characterized reduction. The present data, while not sufficient for unique identification of defects causing various peaks, do strongly suggest that the motion of interstitial cations is involved and that some combination of defects occurs upon reduction of Cr- or Ni-doped rutile.

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Ionic Thermocurrents in Dielectrics*†

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The ionic thermoconductivity (ITC) method, consisting of the study of the thermally activated release of dielectric polarization, is studied in great detail in alkali halide crystals. The (divalent metal ion, cation vacancy) dipoles give rise to an ITC band below 0°C, whose area is proportional to the polarizing field. The activation energy for dipole orientation can be obtained with an accuracy of 0.1%, when there are no overlapping bands. It is shown that the sensitivity of the ITC in detecting small contributions to the polarization (down to 2×10^{15} dipoles per cm^3) or in separating overlapping relaxation processes is greater than that of methods presently employed. The solubility of the impurities can be studied by measuring the ITC of samples subjected to annealing at a fixed temperature. Intense ITC bands appearing in KCl between 280 and 430°K are probably due to contact effects. Measurements on other substances such as quartz, calcite, and Teflon show that by means of a single ITC measurement one obtains a complete qualitative picture of the polarization in a dielectric.

1. INTRODUCTION

THE dielectric relaxations in solid materials are detected in general by means of dielectric-loss measurements: alternating electric fields with frequencies ranging from 10^{-1} to 10^{12} cps have been employed on different types of solids in a very broad range of temperatures.[1] In the case of the dipolar relaxation the maximum of the dielectric loss occurs at the resonance frequency ω_0, inversely proportional to the relaxation time of the dipole at the temperature of the measurements [$\tau(T)=\tau_0\exp\{E/kT\}$]. By measuring the τ at different temperatures one obtains the characteristic parameters of the dipoles, i.e., τ_0 and E.

In some cases, when the relaxation time of the dipoles is of the order of a few seconds, their relaxation can be studied by measuring the charging and discharging current of the dielectric in a constant electric field, at constant temperature.[2] When a static field $\mathcal{E}_p$ is suddenly applied to the dielectric, the kinetics of orientation of the dipoles are of the first order, provided one can neglect their mutual interactions. In this case too, the parameters τ_0 and E can be obtained from a series of isothermal measurements.

Recently a new method has been proposed (ionic thermo-currents: ITC) which gives a complete picture of the temperature-dependent relaxations and allows the parameters τ_0 and E to be obtained by means of a single measurement.[3] The purpose of this paper is to explain in detail the method and to show how it works when applied to the case of alkali halides. The effect of thermal treatments and the ITC of other dielectrics will also be considered.

Let us consider for the moment an ideal dielectric, containing only one type of noninteracting dipoles of moment p and relaxation time τ (Fig. 1): (1) In the absence of an electric field the dipoles are oriented randomly. (2) If one applies an electric field $\mathcal{E}_p$ at the temperature T_p for an interval of time $t_p\gg\tau(T_p)$, the dipoles will be polarized at saturation and in the meantime an exponential current decay will be observed.

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