

Resonance Modes at Defects in Crystalline Quartz*

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The Raman spin-lattice relaxation time T_{1R} for the oxygen divacancy (E_1') center in synthetic crystalline quartz measured in applied magnetic fields of 3 kOe is accurately given by

$$\frac{1}{T_{1R}} = B \frac{e^{x_1}}{(e^{x_1}-1)^2} + C \frac{e^{x_2}}{(e^{x_2}-1)^2} + D e^{-x_3},$$

where $B=0.25 \text{ sec}^{-1}$, $C=250 \text{ sec}^{-1}$, and $D=300\,000 \text{ sec}^{-1}$, and the characteristic frequencies have the corresponding temperatures of $x_1 T = 20 \pm 2^\circ\text{K}$, $x_2 T = 125 \pm 10^\circ\text{K}$, and $x_3 T = 1400 \pm 300^\circ\text{K}$. The two lower frequencies are interpreted in terms of mechanical resonances localized at each center and having large resonant amplitudes. The highest frequency is tentatively associated with some of the optical modes of the SiO_2 lattice. There is no evidence for relaxation by the acoustic modes having the normal Debye cutoff.

INTRODUCTION

A RECENT paper¹ presented a rather extensive set of data on relaxation of E' centers in synthetic crystals of quartz showing an unusual temperature dependence. A model was discussed in which the local strain at each defect center is strongly affected by the presence of localized motion of the defect atoms having characteristic resonance frequencies at small fractions of the Debye frequency. The theoretical expressions used to fit the data were derived on the assumption that the motion at the characteristic frequencies was heavily damped. They gave a T^3 dependence for temperatures above the value corresponding to each characteristic frequency. Since then, measurements² have been made of relaxation of E' centers in vitreous silica. Those data cannot be fitted acceptably by the theoretical expressions for heavy damping but are well fitted by expressions derived on the usual assumption of lattice dynamic calculations³⁻⁵ made for a harmonic lattice. Thus, the resonance modes localized at defects in vitreous silica involve enhanced amplitudes at the characteristic resonance frequencies. More data were needed to decide in the case of crystalline SiO_2 .

It is the purpose of this note to present more complete relaxation data on the oxygen-divacancy (E_1') center in synthetic crystalline quartz and an interpretation of those data in terms of large amplitude motion in the resonance modes of the defect center.

METHOD

The spin relaxation time constant τ was measured again at 9 Gc/sec in one of the samples previously

described.¹ Lattice temperature was varied from 4.2 to 250°K. Our usual inversion-recovery technique was used with the modification⁶ which allowed accurate values to be taken at closely spaced temperatures over the whole range.

In order to obtain the Raman relaxation data, the value of $1/T_{1D}$ was subtracted from each measured value of $1/\tau$. The direct process had been previously determined¹ to be $1/T_{1D} = 1.1(10^{-3})T$.

The calculation of the transition probability for the Raman relaxation involves a complicated sum involving the fourth power of the local strain. The sum is taken over all the lattice modes, where the strain factor is expected to have a peak in the region of each of the characteristic frequencies. An illustration of the strain factor for a grossly simplified model was given in Fig. 5 of Ref. 1. The sum is replaced by a series of simple, definite integrals; in the region of a characteristic frequency, the strain factor is replaced by its peak value for the appropriate frequency interval. If the peak local strain is enhanced sufficiently, the integral involving it dominates the sum. The Raman relaxation then has the form

$$1/T_{1R} = B \exp(x_i) / (\exp(x_i) - 1)^2, \quad (1)$$

where $x_i = \hbar\omega_i/kT$. The above expression corresponds to $n_i(n_i+1)$, where n_i is the occupation number of phonons of frequency ω_i . The form is this simple because the process of relaxation involves the creation and the destruction of phonons at ω_i only.

RESULTS

The Raman relaxation times are plotted in Fig. 1. All the data taken are plotted, with the vertical bars indicating the statistical accuracy of about ten percent for each point.

It is clear in Fig. 1 that $1/T_{1R}$ has a temperature dependence which fluctuates between T^2 and higher powers of T . Therefore, one or more of the T^3 functions

⁶ D. W. Feldman, R. W. Warren, and J. G. Castle, Jr., Phys. Rev. 135, A470 (1964).

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¹ J. G. Castle, Jr., D. W. Feldman, P. G. Klemens, and R. A. Weeks, Phys. Rev. 130, 577 (1963).

² J. G. Castle, Jr., and D. W. Feldman, J. Appl. Phys. (to be published).

³ A. A. Maradudin, *Astrophysics and the Many Body Problem* (W. A. Benjamin, Inc., New York, 1963), p. 107-320.

⁴ P. Dawber and R. Elliott, Proc. Roy. Soc. (London) A273, 222 (1962).

⁵ P. G. Klemens, Phys. Rev. 122, 443 (1961).

used previously¹ does not give an adequate fit to the data.

All the data below 150°K are accurately fitted by a sum of two terms of the form of Eq. (1) involving only four adjustable parameters; this is shown in detail in Figs. 2 and 3. The two characteristic frequencies for the best fit correspond to $20 \pm 2^\circ\text{K}$ and $125 \pm 10^\circ\text{K}$.

The additional relaxation observed above 150°K can be represented by a term in $1/T_{1R}$ of several forms; $x^{-7} J_6(x)$, or $x^{-9} J_8(x)$, or $\exp(-x)$, where xT is another characteristic temperature with a value of at least 1100°K.

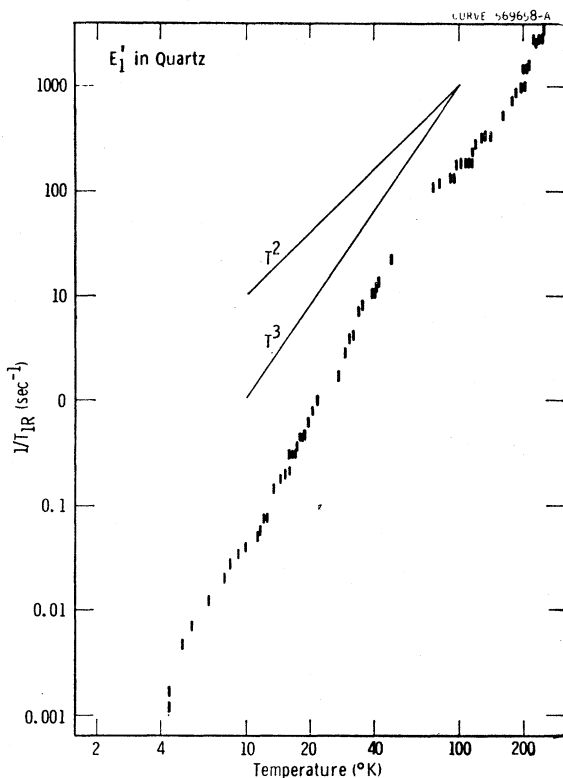


FIG. 1. Reciprocal of Raman relaxation time versus temperature, measured at 3 kOe.

DISCUSSION

The spin attached to the silicon atom in an oxygen divacancy (E_1') is apparently relaxed at temperatures from 4°K up to about 150°K by just two mechanisms, each contributing a term of the form of Eq. (1). The significance of this form is that the strain due to motion at ω_i is very large. The Raman relaxation produced by strain at ω_i completely overshadows the relaxation due to all the other frequencies up to the Debye limit. An estimate from a complete sum of terms in $1/T_{1R}$ indicates that the strain modulus at ω_i must be at least a factor of 10 larger than that due to normal phonons, in order for the T^3 terms to be overshadowed. This Raman relaxation due to enhanced strain at a charac-

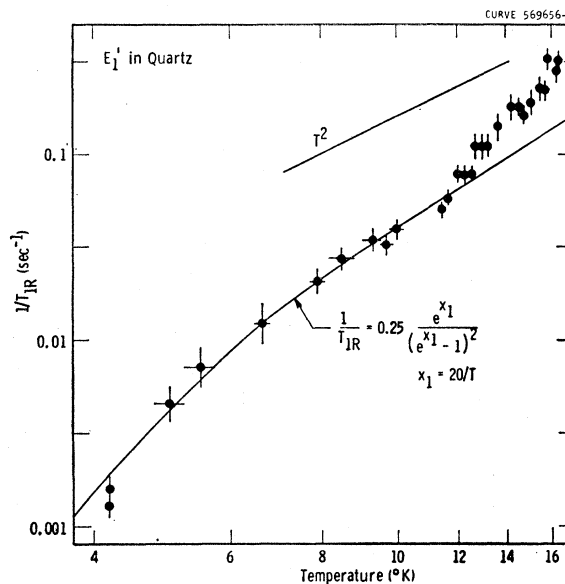


FIG. 2. Raman relaxation in the low-temperature region.

teristic frequency of vibration is different from the Orbach process⁷ in which the interaction per unit strain is enhanced at a characteristic frequency of electron excitation of the center.

The additional relaxation which appears at temperatures above 150°K may be due to the normal type of Raman relaxation, say $x^{-9} J_8(x)$ with xT being an effective Debye limit. However, to fit the few data points well requires a value for xT which is significantly higher than the specific heat value of about 750°K. Therefore,

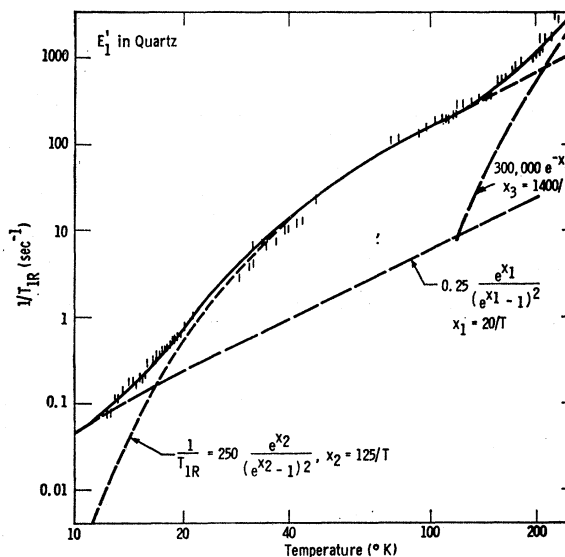


FIG. 3. Raman relaxation in the high-temperature region. The solid curve is the sum of the dashed curves.

⁷ R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

we prefer an explanation which does not involve the acoustic modes of the lattice.

A term of the form of Eq. (1) with $x_3T=1400^\circ\text{K}$ could also be written as $D \exp(-x_3)$. Such an expression would be expected from any process involving optical lattice modes. In fact, the value we find for x_3T is consistent with the energies observed in Raman spectra and infrared spectra of quartz.⁸⁻¹⁰

CONCLUSIONS

The spin-lattice relaxation of the spin attached to the silicon atom in the oxygen divacancy (E_1') center in crystalline quartz is given accurately from 1.3 to 250°K by the expression

$$1/T_1 = AT + B(e^{x_1}/(e^{x_1}-1)^2) + C(e^{x_2}/(e^{x_2}-1)^2) + De^{-x_3},$$

⁸ A. Kats, thesis, University of Delft, 1961 (unpublished).

⁹ W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961).

¹⁰ D. A. Kleinman and W. G. Spitzer, Phys. Rev. **125**, 16 (1962).

where $A=0.011 \text{ sec}^{-1} \text{ }^\circ\text{K}^{-1}$, $B=0.25 \text{ sec}^{-1}$, $C=250 \text{ sec}^{-1}$, $D=300\,000 \text{ sec}^{-1}$, $x_1T=20\pm 2^\circ\text{K}$, $x_2T=125\pm 10^\circ\text{K}$, and $x_3T=1400\pm 300^\circ\text{K}$. The three exponential factors correspond respectively to characteristic frequencies of motion at the defect of 4.1×10^{11} , 2.5×10^{12} , and 2.9×10^{13} cps. The dominance of the first two terms shows the existence of large strain amplitudes at the defect for the frequencies of these two localized resonance modes. The last term indicates the probable role of optical modes of the normal lattice.

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Surface Ionization of Some Rare Earths on Tungsten*

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The surface ionization of Gd, Er, and Yb atomic beams on a clean (112) tungsten surface has been studied in an ultrahigh-vacuum mass spectrometer. For the first time, the absolute ionization efficiencies have been determined as a function of surface temperature. The degree of ionization α was found to follow the general form of the Saha-Langmuir equation $A\alpha = Ae^{-E/kT}$. The magnitudes of A and E , however, are not consistent with the predicted values. Values of A and E are summarized below:

Material	Experimental values		Theoretical values	
	E (eV)	A	E (eV)	A
Gadolinium	1.88 ± 0.02	38 ± 9	1.31 ± 0.07	1.06
Erbium	1.38 ± 0.02	2.1 ± 0.5	1.23 ± 0.10	1.08
Ytterbium	1.84 ± 0.01	8.5 ± 1.8	1.37 ± 0.07	2.00

The Saha-Langmuir theory was found to be inadequate for the surface ionization of complicated atoms *in beams* on single-crystal tungsten surfaces. This work makes clear the necessity for more detailed theoretical studies of the process. An auxiliary measurement of the work function of the (112) surface of tungsten yielded 4.85 ± 0.07 eV.

I. INTRODUCTION

A. Foreword

THE phenomenon of surface ionization (SI) has been studied for the alkali metals on tungsten surfaces since 1923. Zandberg and Ionov¹ have pre-

sented a thorough review which includes critiques of the major experiments in the light of present knowledge. Kaminsky² has written a useful summary of the experimental work in SI.

Both the temperature dependence and the absolute magnitude of SI efficiency in the *very low* efficiency case have not adequately been studied. The agreement of the temperature dependence with theoretical predictions is not conclusive. *Absolute* efficiency work in the very low efficiency range has been limited to copper and

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¹ E. Ya. Zandberg, and N. I. Ionov, Usp. Fiz. Nauk **57**, 581 (1959) [English transl.: Soviet Phys.—Uspekki **67**, 255 (1959)].

² M. Kaminsky, Ergeb. Exakt. Naturw. (to be published).