Temperature Dependence of the Width and Position of the $^2E \rightarrow {}^4A_2$ Fluorescence Lines of Cr³⁺ and V²⁺ in MgO†

G. F. Imbusch, W. M. Yen, and A. L. Schawlow

Stanford University, Stanford, California

AND

D. E. McCumber and M. D. Sturge

Bell Telephone Laboratories, Murray Hill, New Jersey 07971

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The energy levels of an impurity ion in a solid are in general shifted and broadened by thermal vibrations of the host lattice. A study of these effects in a simple system can lead to some understanding of the phonon-impurity interaction. This paper reports measurements of the width and positions of the sharp fluorescence lines of two $(3d)^3$ ions in MgO between 4.2°K and room temperature. A semiempirical model is used to calculate the temperature dependence of the width and position from the vibrational structure associated with the sharp no-phonon line. The shift agrees well with theory but the linewidth deviates somewhat at low temperatures.

INTRODUCTION

THE temperature dependence of the width and position of the R lines of ruby has been studied by several workers.[1-4] Attempts have been made with moderate success to explain theoretically the observed broadening and shift to the red.[4-7] The basic inadequacy of the models utilized is that they fail to reflect the detailed structure of the crystal lattice, which in ruby has low (trigonal) symmetry and ten ions per unit cell. A more theoretically tractable system is that of MgO:Cr³⁺. The MgO lattice is cubic with two ions per unit cell; the impurity Cr³⁺ ions substitute for Mg²⁺ ions. Those impurities which occupy cubic sites give rise to a single sharp fluorescence line at 6981 Å; those others which occupy sites made noncubic by nearby charge-compensation defects have more complicated spectra. The complications due to charge compensation do not appear if the impurity is the isoelectronic V²⁺ ion. This ion has a sharp fluorescence line at 8697 Å which arises from the $^2E \rightarrow {}^4A_2$ transition, as does the 6981-Å line of Cr³⁺.

We have measured the width and shift of the 6981-Å line of Cr³⁺ and the 8697-Å line of V²⁺ in MgO from 4.2°K to room temperature. We compare the results with a simple model in which an effective density of states for phonons interacting with the impurity is deduced from the vibrational structure associated with

the sharp line of the V²⁺ spectrum. The observed shift with temperature is in good agreement with the model. The observed linewidth deviates from the model slightly at low temperatures, where it is found to be slightly larger than predicted, even after the residual width at 4.2°K (attributed to strain broadening) has been subtracted out. This deviation is specimen-dependent and is probably due to a temperature dependence of the strain broadening, possibly connected with low-frequency vibrations of dislocations.

EXPERIMENTAL

Crystals of chromium- and vanadium-doped MgO used in this investigation were obtained from the Norton Company and had dopings of 0.05%. In the case of vanadium-doped MgO the vanadium ions exist in V³⁺ and V²⁺ states in the crystal. Most of the ions are in the V³⁺ state and the fluorescence at 8697 Å due to V²⁺ is very weak. Heating for eight hours in a hydrogen furnace at 1200°C increases the V²⁺ concentration by a factor of about a hundred.[8] Both the Cr³⁺ line at 6981 Å and the V²⁺ line at 8697 Å arise from $^2E \rightarrow {}^4A_2$ transitions, are magnetic dipole, and are much
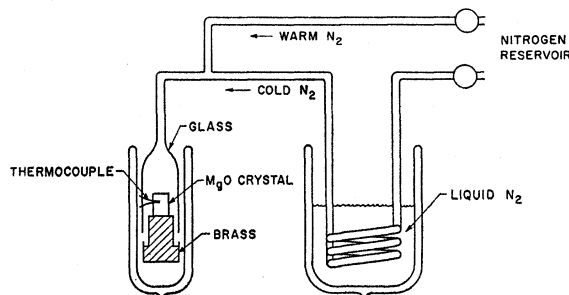
[1] K. S. Gibson, Phys. Rev. 8, 38 (1916).
[2] H. K. Paetzold, Z. Physik 129, 123 (1951).
[3] A. L. Schawlow in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1962), p. 50.
[4] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).
[5] A. Kiel, Phys. Rev. 126, 1292 (1962).
[6] R. H. Silsbee, Phys. Rev. 128, 1726 (1962).
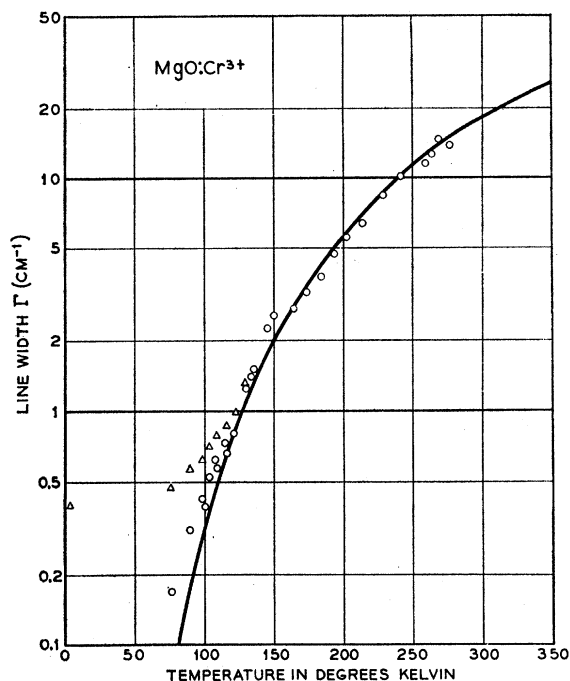[7] R. J. Adler, Bull. Am. Phys. Soc. 7, 600 (1962).

FIG. 1. Schematic diagram of the apparatus.

[8] M. D. Sturge, Phys. Rev. 130, 639 (1963).

FIG. 2. Full width at half-maximum of the 6981-Å fluorescence line of MgO:Cr³⁺, as a function of temperature. Δ, experimental points; o, corrected for temperature-independent strain broadening as explained in the text. The curve is calculated from Eq. (2), with $\rho(\omega)$ determined from Fig. 7 and $\bar{\alpha}$ chosen to give the best fit with experiment.

weaker than the corresponding ruby R lines. Measurements of width and shift were made in emission. It was not possible to get accurate data above room temperature because of the weakness of the fluorescence.

The crystal was placed in front of a Jarrell-Ash high resolution scanning spectrometer, and a liquid-nitrogen-cooled RCA 7102 photomultiplier was used as a detector. Temperatures in the range 90°K to room temperature were obtained with the apparatus shown in Fig. 1. Nitrogen gas, precooled by circulation through liquid nitrogen, was blown across the crystal; nitrogen gas at room temperature was mixed with the cold gas to obtain the intermediate temperatures. Temperatures were measured by a thermocouple inserted in the crystal. Liquid oxygen, liquid nitrogen, and liquid helium were also used as direct coolants. To excite the fluorescence four Sylvania 150-W "Tru-flector" projection lamps were used. The lamps were immersed in either distilled water or in copper-sulfate solution to cool the lamps and to prevent infrared heating of the sample. A mercury arc lamp was sometimes used to excite fluorescence at helium temperatures.

RESULTS

Figure 2 shows the temperature dependence of the width of the Cr³⁺ 6981-Å line. As the temperature approaches zero the width approaches a finite value

of approximately 0.4 cm⁻¹. This residual width presumably results from random static strains in the crystal.[3,9] An isotope shift will contribute only a small effect, as single isotopes are dominant in both Cr and V. If the strains are *microscopic* and randomly distributed, the shape of the line as T approaches zero should be Gaussian. At 4.2°K where thermal affects are negligible, the actual experimental shape is almost, but not quite, Gaussian. This deviation probably results from macroscopic strains. At room temperature where the thermal broadening is much greater than the residual strain width, the shape is Lorentzian. At intermediate temperatures it is a mixture; the Gaussian character increases as the temperature is lowered. his agrees with the theoretical result[4] that the interaction of the lattice vibrations with the paramagnetic ion causes a Lorentzian broadening of the spectral lines at high temperatures.

To separate the residual or zero-temperature width from the values obtained at higher temperatures, we assumed that the residual width was completely Gaussian and the temperature-dependent width was completely Lorentzian. Using the numerical tables of Posener[10] to separate the Gaussian and Lorentzian components, we determined the corrected temperature-dependent linewidths. The corrected full width at half-maximum of the Cr³⁺ 6981-Å line is plotted against temperature in Fig. 2. The corresponding plot for the V²⁺ 8697-Å line appears in Fig. 3.

Figure 4 shows the shift *below* its position at 4.2°K of the peak of the 6981-Å line of MgO:Cr³⁺. Figure 5 shows the same for MgO:V²⁺. As in the case of ruby,[2]
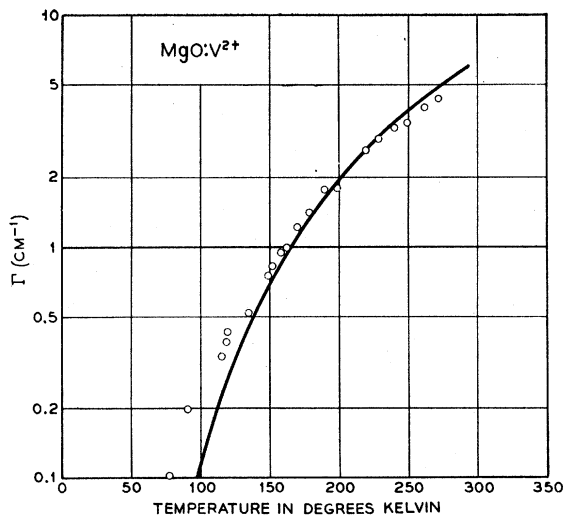

FIG. 3. Width of the 8697-Å line of MgO:V²⁺ as a function of temperature. Points are corrected for strain broadening. Curve calculated from Eq. (2) as in Fig. 2.

[9] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. 122, 1469 (1961).
[10] D. W. Posener, Australian J. Phys. 12, 184 (1959).

thermal expansion of the lattice can only account for about 10% of the shift; moreover, it would act to shift the line in the sense opposite to that observed.

THEORETICAL

McCumber and Sturge[4] have calculated the temperature dependence of the linewidth Γ and frequency shift $\Delta\omega$ under the assumption that the phonon spectrum approximates a Debye spectrum of acoustic phonons. In fitting the observed data, they adjusted both the strength of the relevant phonon-impurity coupling constants and the Debye temperature characterizing the phonons. If the assumption of a Debye spectrum is not made but if it is assumed that the phonon-impurity interaction results from linear and quadratic components of a single operator S characterizing the local lattice distortion or strain in the neighborhood of the impurity, their formulas generalize to[11]

$$\Delta\omega(T) = \alpha \int_0^\infty \frac{d\omega}{2\pi} \rho(\omega)n(\omega), \qquad (1)$$

$$\Gamma(T) = \bar\alpha \int_0^\infty \frac{d\omega}{2\pi} [\rho(\omega)]^2 n(\omega)[1+n(\omega)]. \qquad (2)$$

Here $n(\omega) = [\exp(\omega\hbar/kT)-1]^{-1}$ and $\rho(\omega)$ is an *effective* density of phonon states. Typically if s_k is a dimension-
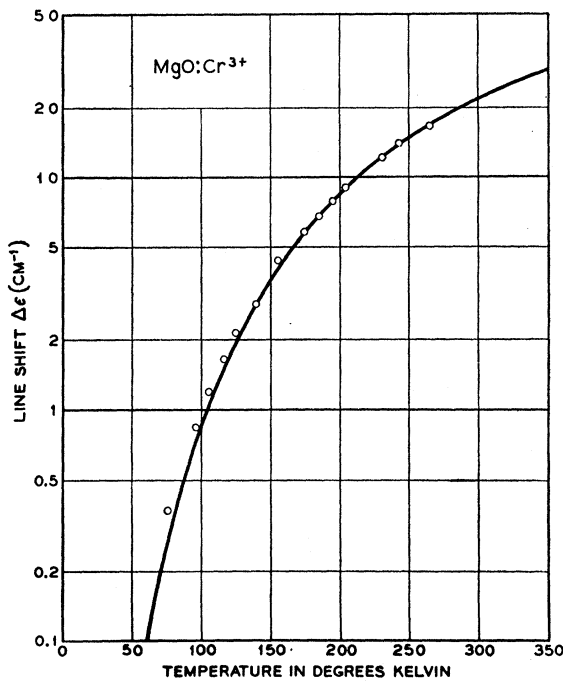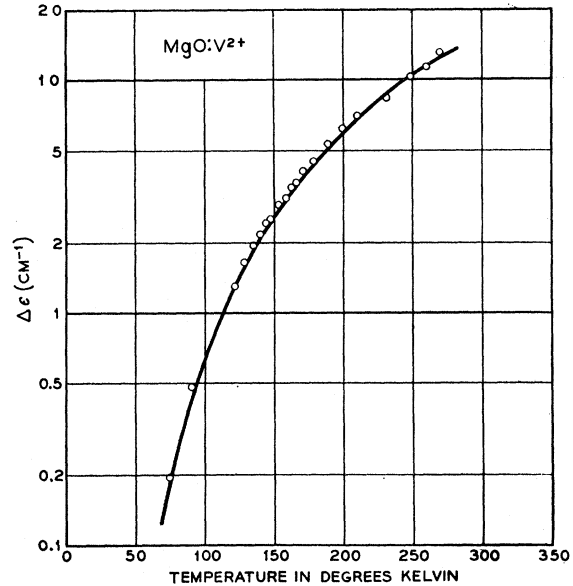

Fig. 5. Shift of the 8697-Å line of MgO:V^{2+} below its position at 4.2°K. The curve is calculated from Eq. (1).

less coupling parameter describing the contribution to the local lattice strain S of the phonon of wave vector $\mathbf{k}$ and frequency ω_k, then

$$\rho(\omega) = \sum_k |s_k|^2 2\pi\delta(\omega-\omega_k). \qquad (3)$$

If s_k were identically unity, $\rho(\omega)$ would be simply the phonon density of states. In fact, it is that density of states weighted by the coupling parameters $|s_k|^2$.

The main problem in applying Eqs. (1) and (2) is what to take for $\rho(\omega)$, since the phonon spectrum and the coupling constants s_k are generally unknown. McCumber and Sturge[4] assumed a Debye spectrum of acoustic phonons. For this case, typically[12]

$$s_k = [k\hbar/2\rho_m V\bar v]^{1/2}$$

and

$$\rho(\omega) = \hbar\omega^3/2\pi\rho_m\bar v^5 \quad \text{for} \quad 0 \leq \omega \leq \omega_D, \qquad (4)$$

where $\hbar\omega_D/k = \theta_D$, an effective Debye temperature. In these equations $\bar v$ is the average sound velocity, ρ_m is the mass density of the crystal lattice, and V is the crystal volume. When used in Eqs. (1) and (2), this density gives

$$\Delta\omega(T) = \frac{\alpha\hbar}{(2\pi)^2\rho_m\bar v^5} \int_0^{\omega_D} d\omega \frac{\omega^3}{[\exp(\hbar\omega/kT)-1]}, \qquad (5)$$

$$\Gamma(T) = \frac{\bar\alpha}{2\pi}\left(\frac{\hbar}{2\pi\rho_m\bar v^5}\right)^2 \int_0^{\omega_D} d\omega \frac{\omega^6 \exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT)-1]^2}. \qquad (6)$$

Fig. 4. Shift of the peak of the 6981-Å line of MgO:Cr^{3+} below its position at 4.2°K. The curve is calculated from Eq. (1).

[11] D. E. McCumber, J. Math. Phys. 5, 222 (1964).

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[12] The operator S constructed from these s_k may be more easily interpreted in terms of local lattice distortions than can the corresponding operator in Ref. 4 where the s_k are not dimensionless.
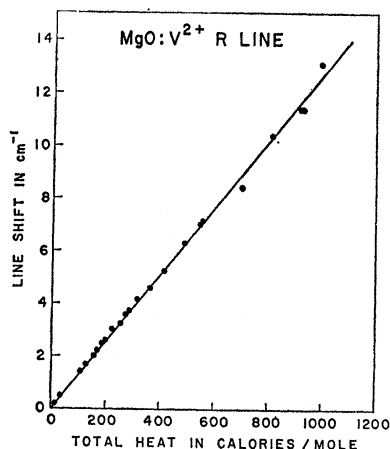
FIG. 6. Shift of the 8697-Å line of MgO: V^{2+} plotted against the total heat of MgO calculated from the specific heat data of Ref. 14.

The expression (5) for $\Delta\omega(T)$ is the same, apart from a multiplicative constant and for a certain arbitrariness θ_D, as that for the total heat. Thus a Debye model would lead us to expect a correlation between $\Delta\omega(T)$ and the total heat, which is indeed observed.[13] The normalized line shift for MgO:V^{2+} is plotted against the total heat in Fig. 6.

The observed line shift and linewidth can be fitted moderately well by Eqs. (5) and (6). However, as in the case of ruby it is necessary to use a value $\theta_D = 650°K$ which is rather lower than that $(750°K)$ determined from the specific heat.[14] Since it is well known that the phonon spectra of diatomic lattices do not resemble the Debye spectrum, a more realistic choice of $\rho(\omega)$ should be employed. The vibrational structure associated with the sharp "no-phonon" line of the impurity spectrum reflects an effective (coupling-weighted) phonon spectrum and can be used to establish an approximation for $\rho(\omega)$ independent of the arbitrary parameter θ_D in the Debye model of McCumber and Sturge.[4]

The sharp line in the impurity spectrum corresponds to a pure electronic transition; it has the same position in absorption and emission. In addition to this "no-phonon" transition, transitions can occur in which a phonon (as well as a photon) is emitted or absorbed. Such transitions are responsible for the vibrational structure accompanying the no-phonon line. At low temperatures only phonon emission is possible, so the vibrational structure is to the blue of the no-phonon line in absorption and to the red in emission. The probability for such transitions is determined primarily by interactions which are linear in the lattice distortion

[13] A. L. Schawlow, Proceedings of the Third International Conference on Quantum Electronics, Paris, 1963 (to be published).

[14] The specific heat data of W. F. Giauque and R. C. Archibald [J. Am. Chem. Soc. 59, 561 (1937)] fit the Debye function for $\Theta_D = 750°K$ quite accurately as temperatures below 270°K. At higher temperatures substantial deviations are observed, confirming the inadequacy of the Debye model as a description of the phonon spectrum of MgO. In this MgO differs from Al_2O_3, for which the specific heat fits the Debye function well from 50° to 1000°K (see Ref. 4).

in the neighborhood of the impurity. If again only the single operator S is relevant to the phonon-impurity coupling, the intensity of the vibrational structure at very low temperatures is proportional to[11]

$$I(\omega) = |C|^2\rho(\omega)/(\hbar\omega)^2 + (\text{multiphonon terms}), \quad (7)$$

where the angular frequency ω is measured relative to the no-phonon line, and C is the constant appearing in Eq. (8) below.

The vibrational structure associated with the 8697-Å line of MgO:V^{2+} in emission is shown in Fig. 7. The corresponding vibrational structure for MgO:Cr^{3+} is obscured by strong emission from chromium ions at noncubic sites (which exist because charge compensation of the Cr^{3+} ion is necessary) and has not been used in this analysis. In Fig. 7 peaks at about 270 cm^{-1}, 430 cm^{-1}, 490 cm^{-1}, and 540 cm^{-1} are seen. The 490 cm^{-1} peak presumably corresponds to an optical branch of the MgO phonon spectrum, as the *reststrahl* is in this region.[15] Probably the 270 cm^{-1} and possibly the 430 cm^{-1} peaks correspond to acoustic phonons at the zone boundary, where the density of states is greatest. The 540 cm^{-1} peak probably corresponds to the emission of two acoustic phonons. Further weak structure due to two-phonon processes is seen still further to the red. Dropping the 540 cm^{-1} peak and treating the rest of the structure shown in Fig. 7 as being due to single-phonon processes, we derive with the aid of Eq. (7) the effective phonon density $\rho(\omega)$ shown in Fig. 8. When this result is used in Eqs. (1) and (2), we obtain the theoretical curves shown in Figs. 2, 3, 4, and 5. The constants α and $\bar{\alpha}$, which relate to the strength of the phonon-impurity interaction, are chosen to give the best fit with experiment for each curve.

The line-shift data of Figs. 4 and 5 agree remarkably well with the theoretical curve. The fact that the data for MgO:Cr^{3+} agree with the curve calculated from the vibrational structure appropriate to MgO:V^{2+} suggests that the dependence of the phonon-impurity coupling on phonon frequency is the same for both.
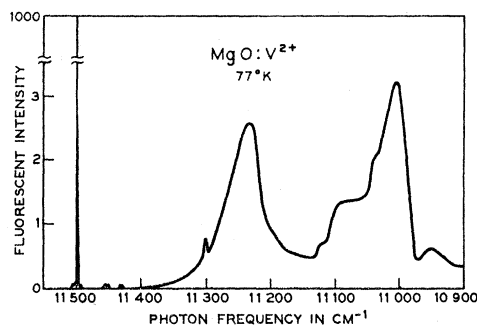

FIG. 7. Vibrational structure associated with the 8697-Å fluorescence line of MgO:V^{2+} (redrawn from Ref. 8).

[15] J. C. Willmott, Proc. Phys. Soc. (London) A63, 389 (1950).

The uncompensated charge on the Cr^{3+} ion does not apparently alter the coupling, except in magnitude.

In Figs. 2 and 3 the linewidth is somewhat larger than predicted at low temperatures. The deviation is comparable to that which obtained in the Debye-phonon fit of McCumber and Sturge for the R lines of ruby.[4] Temperature-dependent strain broadening is probably the cause of the deviation. At no temperature is the deviation from theory more than one-third the residual linewidth at 4.2°K, and the deviation is least in those specimens with the smallest residual linewidth. If we assume that the broadening is primarily due to the strain field of dislocations, a possible mechanism for a temperature dependence of the strain broadening is as follows. A dislocation can vibrate at a frequency determined by the velocity of sound and the (random) separation of pinning points. In MgO this frequency should be in the region 10^8–10^{10} cps, for which $\hbar\omega \ll kT$ if $T \geq 4°$K. When they are coupled to the impurity ion, the dislocation vibrations with frequencies less than the observed linewidth will modify the line shape. If $\hbar\omega \ll kT$, the resulting line will be Gaussian with a width proportional to the coupling strength and to $(kT)^{1/2}$, which temperature dependence is roughly what is observed (after the contribution of the phonons has been subtracted). As we do not know the dislocation density nor the mean separation of pinning points, we cannot calculate precisely the size of the effect to be expected, but the order of magnitude is not unreasonable. Measurements on plastically deformed crystals would provide a test of the theory.

The ratios

$$\alpha(\text{MgO}:\text{Cr}^{3+})/\alpha(\text{M}\alpha\text{O}:\text{V}^{2+}) = 1.4$$

and

$$\bar{\alpha}(\text{MgO}:\text{Cr}^{3+})/\bar{\alpha}(\text{M}\bar{\alpha}\text{O}:\text{V}^{2+}) = 2.5$$

are close to what would be expected from the known shift of the ^2E levels with static strain. The shifts of the R lines with static stress (dilation) are $9.7\pm0.3 \times 10^{-11}$ cm^{-1}/dyn/cm^2 for $\text{MgO}:\text{Cr}^{3+}$ and $8.3\pm0.3 \times 10^{-11}$ cm^{-1}/dyn/cm^2 for $\text{MgO}:\text{V}^{2+}$.[9,16] From the model implicit in Eqs. (1), (2), and (7) we would roughly expect the α ratio to be $(9.7/8.3)^2 = 1.35\pm0.15$ and the $\bar{\alpha}$ ratio to be $(9.7/8.3)^4 = 1.8\pm0.4$.

DISCUSSION

In the model from which Eqs. (1), (2), and (7) were derived,[11] it is convenient to introduce an operator

$$\Omega(t) = \Omega_0 + CS(t) + D[S(t)]^2 \qquad (8)$$

which measures the frequency separation, as a function of the instantaneous lattice-strain field $S(t)$, of the initial and final impurity levels responsible for the observed spectral line. The frequency of the no-phonon
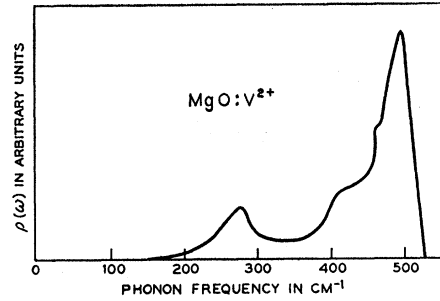

FIG. 8. Effective density of states $\rho(\omega)$ for $\text{MgO}:\text{V}^{2+}$ estimated from Fig. 6 using Eq. (5). Spectrometer dispersion and photomultiplier response are corrected for.

line is related to the average value of the operator (8) in an ensemble describing the impurity plus lattice. Since positive or negative excursions of $S(t)$ relative to any temperature-independent mean strain are equally likely, only the quadratic terms in Eq. (8) contribute to the temperature-dependent line shift of Eq. (1). The Lorentz width Γ in Eq. (2) arises from Raman scattering of phonons by the impurity. The integrand of Eq. (2) is easily understood in this model: the probability for absorbing a phonon of frequency ω is $\rho(\omega)n(\omega)$, that for subsequently emitting such a phonon is $\rho(\omega)[1+n(\omega)]$. The linewidth can alternatively be interpreted in terms of the secular perturbation model of Bloembergen, Purcell, and Pound.[17] In either case only those components of the phonon-impurity interaction in Eq. (8) contribute which are quadratic in the strain $S(t)$.

Although for the simple model used in the derivation of Eqs. (1), (2), and (7) the same effective phonon density $\rho(\omega)$ appears in each equation, a detailed analysis based upon a more elaborate model would distinguish between the densities relevant to each equation. The central assumption in our fitting procedure is that to a good approximation we may assume the different $\rho(\omega)$'s equal to within a multiplicative constant.[18] The validity of this approximation for $\text{MgO}:\text{V}^{2+}$ and $\text{MgO}:\text{Cr}^{3+}$ is confirmed by the good fit to experimental data which we have already noted. The same approximation does *not* give a comparably good fit to line-shift and linewidth data for the isoelectronic impurity sequence V^{2+}, Cr^{3+}, Mn^{4+} in corundum ($\alpha-\text{Al}_2\text{O}_3$). There is some theoretical evidence (to be discussed in greater detail by some of us in a subsequent publication) that this is due to the low (trigonal) crystal symmetry of $\alpha-\text{Al}_2\text{O}_3$, whereas

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[16] M. D. Sturge, Phys. Rev. 131, 1456 (1963).

[17] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948); D. E. McCumber, Phys. Rev. 133, A163 (1964).

[18] The simple model based on Eq. (8) predicts $\alpha = D/2$ and $2 \geq 2\bar{\alpha}/\alpha^2 \geq 1$; a more elaborate model taking anisotropy into account would predict $2\bar{\alpha}/\alpha^2 \gtrsim 0.2$. From the fit of theory to experiment we find $2\bar{\alpha}/\alpha^2 = 0.34$ for $\text{MgO}:\text{V}^{2+}$ and 0.41 for $\text{MgO}:\text{Cr}^{3+}$.

MgO has relatively high (cubic) symmetry. In any case the vibrational spectra in $\alpha-Al_2O_3$ are considerably more complicated than the MgO:V^{2+} spectrum indicated in Fig. 6. It is in fact difficult (especially for $\alpha-Al_2O_3$:Mn^{4+}) to separate the effective "one-phonon" density of states from the multiphonon contributions to the vibrational structure.

If and when the lattice spectrum of MgO is determined, the MgO:V^{2+} and MgO:Cr^{3+} cases seem to be promising ones for an attempt to calculate the impurity-phonon interaction from first principles. Not only is the lattice an exceptionally simple one, but the point-charge model has been shown to give quantitatively correct results for the effect on the ^2E state of static strain.[9,16] It remains to be seen if equally good agreement can be obtained for interaction with the phonons.

ACKNOWLEDGMENTS

Instability in Crystals and Thermal Expansion Coefficients

MARVIN ARENSTEIN*

Autonetics Research Center, Anaheim, California

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An analysis is made of the Grüneisen parameter $\gamma_i = -d \ln\nu_i/d \ln V$, where ν_i is a normal mode frequency and V is the volume for certain ideal and real crystals. It is shown that negative thermal expansion or anomalous positive expansion in a solid is a possible result of an approach to instability of the modes of vibration.

A. INTRODUCTION

THIS paper is an extension of two previous papers,[1] hereafter referred to as I and II. An analysis of the expressions for the Grüneisen parameter derived in these papers indicates the conditions under which a crystal can have negative thermal expansion coefficients or anomalous positive thermal expansion coefficients. Recent experimental evidence[2] shows that certain crystals, such as silicon, ZnS, InSb, SiO_2, and AgI, undergo negative thermal expansion. Blackman[3] has considered an ionic zincblende structure and found from an analysis of the elastic constants that it would have a negative expansion at low temperatures. It was concluded that open structures, those with a coordination number of four and having a very low shear elastic constant (C_{44}), should have a negative thermal expansion.

In I, we considered some ideal cubic crystals having short-range interactions, such as a two-dimensional diatomic square lattice and a simple cubic lattice. It was found that they exhibited negative expansion when they were unstable or approached instability.[4] The following analysis suggests that the instability or approach to instability may be the cause for negative expansion or anomalous positive expansion in a real crystal. Such a possibility is interesting since the explanations for the melting of solids[5] and the ferroelectric transition[6] have been sought in the approach to instability of the acoustic modes in the former situation and the transverse optical modes in the latter.

The volume coefficient of thermal expansion β of a crystal can be written as

$$\beta = (X\Sigma_i\gamma_i\partial E_i/\partial T)/V, \qquad (1)$$

with γ_i the Grüneisen parameter given as

$$\gamma_i = -d \ln\nu_i/d \ln V. \qquad (2)$$

Here X is the isothermal compressibility, V is the volume, E_i is the thermal energy $\{h\nu_i/[\exp(h\nu_i/kT)-1]\}$, and ν_i is a normal mode frequency. T, h, and k have their usual meaning and the sum over i is to be taken over all normal modes. Since X, V, and $\partial E_i/\partial T$ are always positive, it can be seen that if γ_i is negative for a large number of frequencies or if γ_i is very large and negative ($\gamma_i \rightarrow -\infty$) for just a few frequencies, then β will be negative. Expressions for γ_i have been found for several ideal lattices and for a real crystal such as NaCl.[1] It is expected that γ_i will take the same form for many molecular and ionic solids. It can be shown that the conditions under which the lattice approaches nega-

* Present address: 1352 Findlay Avenue, Bronx 56, New York.
[1] By paper I, we refer to "Equation of State of Certain Ideal Lattices," Phys. Rev. **131**, 2087 (1963), and by paper II to "Equation of State of Alkali Halides (NaCl)," Phys. Rev. **132**, 73 (1963) both by M. Arenstein, R. D. Hatcher, and J. Neuberger.
[2] R. D. McCammon and G. K. White, Phys. Rev. Letters **10**, 234 (1963).
[3] M. Blackman, Phil. Mag. **3**, 831 (1958).
[4] For a discussion of stability of simple lattices, see M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England 1954), Chap. 3.

[5] M. Born, J. Chem. Phys. **7**, 591 (1939); J. H. C. Thompson, Phil. Mag. **44**, 131 (1952).
[6] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.