Isotope Shift in the R Lines of Chromium in Ruby and MgO*

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At 4.2°K the R lines of chromium in ruby and in MgO exhibit an isotope shift of 0.13 and 0.17 cm^{-1} per unit mass, respectively. This is a much larger value than is found for free atoms of intermediate mass. We consider the possibility that this isotope shift is caused by the interaction of the ion with the vibrating lattice. The ion-phonon interaction causes a frequency shift in these R lines, and this shift depends on the amplitude of vibration of the chromium ion. The lighter chromium isotopes, however, have a larger amplitude of vibration than the heavier isotopes, and consequently the frequency shift varies from isotope to isotope. This leads to an isotope shift. For the R lines of ruby and MgO:Cr^{3+} the isotope shift due to the interaction with the zero-point vibrations is calculated, and is in very good agreement with the experimental values, both in magnitude and direction.

INTRODUCTION

THE effects of vibrations of the host lattice on the sharp optical transitions of impurity ions in a crystal have been the subject of much recent investigation. These effects include a shift and broadening of the lines with increasing temperature,[1-3] the appearance of sidebands,[4-7] and relaxation processes between adjacent levels of the impurity ions. The investigation of such effects may be a fruitful method of probing the vibrational spectrum of the host lattice. Indeed, many of the phenomena which are being considered for investigation by means of the Mössbauer effect can also be investigated by examining the details of the optical spectra of suitable impurity ions imbedded in the lattice.[8]

The impurity ion, then, acts as a probe to detect the effect of the lattice vibrations. However, this ion is generally of different mass and is often bound by a different coupling constant from the regular ions. We then detect not the vibrations of the regular host ions, but rather the vibrations being experienced by the impurity ion. Now the problem of the vibrations of a defect in an otherwise regular lattice has been the subject of much theoretical interest.[9] The defect causes a change in amplitude of the regular modes of vibration and there may be new modes localized around the defect. Many of these effects are susceptible to investigation through examination of sharp optical transitions emitted by the impurity ion. We show here how a consideration of the vibrations of the impurity ion can explain the isotope shift found in the sharp R lines of ruby[10] and MgO:Cr^{3+}.

EXPERIMENTS AND RESULTS

At 4.2°K the thermal broadening of the R lines is negligible and the width is determined by strains in the crystal. The crystal to be examined was placed in a Dewar containing liquid helium and positioned in front of a Jarrell-Ash 1.8-m Ebert recording spectrometer. The lines were measured in emission. An RCA-7102 or RCA-7265 photomultiplier, cooled by liquid nitrogen, was used as a detector. The fluorescence was excited either by a 1000-W water cooled mercury arc lamp or by the simultaneous use of several tungsten filament lamps. Dilute copper sulfate solution was used as a filter in both cases, as it transmits radiation in the region of the absorption bands of the samples investigated.

The R_1 line of ruby is a doublet whose components are separated by 0.38 cm^{-1}. By careful control over the growing process, the strains can be reduced and this separation completely resolved. Close examination, however, reveals asymmetry in the shape of the individual components, Fig. 1.

It was suspected that this asymmetry might be

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[1] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).

[2] A. L. Schawlow, in *Proceedings of the Third International Conference on Quantum Electronics, Paris*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964).

[3] G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).

[4] See, for example, the papers of R. A. Satten, E. Y. Wong, and co-workers. A recent work is I. Richman, R. A. Satten, and E. Y. Wong, J. Chem. Phys. **39**, 1833 (1963).

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[6] G. F. Imbusch and A. L. Schawlow (to be published).

[7] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).

[8] R. H. Silsbee and D. B. Fitchen, Rev. Mod. Phys. **36**, 432 (1964).

[9] See, for example, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by Seitz and D. Turnbull (Academic Press, Inc., New York, 1963), Suppl. 3, for references and historic survey to 1962. Further references are contained in A. A. Maradudin, Rev. Mod. Phys. **36**, 417 (1964).

[10] A. L. Schawlow, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 50.
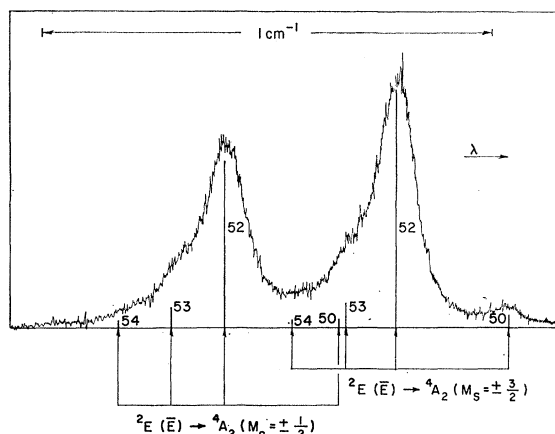
FIG. 1. The R_1 line of ruby showing the two components caused by the ground-state splitting. The fine structure due to the chromium isotopes is indicated.

caused by isotope shift. The most abundant chromium isotopes are[11]: Cr^{50}, 4.3%; Cr^{52}, 83.8%; Cr^{53}, 9.6%; and Cr^{54}, 2.4%. The absence of Cr^{51} suggests that the hump on the long-wavelength side is due to Cr^{50}. The asymmetry on the short-wavelength side would thus be attributed to Cr^{53} and Cr^{54}. By such analysis the positions of the isotope lines were inferred and are indicated on Fig. 1.

Crystals with separated chromium isotopes were grown by one of us (JPR) by a flux method described elsewhere,[12] and the positions of the individual isotope lines were accurately measured. Good agreement was found with the positions inferred from the asymmetry in the crystals of normal isotopic abundance.

Chromium ions at cubic sites in MgO fluoresce in a single R line. It is more difficult to obtain strain-free chromium doped MgO crystals and the line is broader than for ruby. The doping process itself may introduce strains, and empirically the sharpest lines are found in very lightly doped crystals. We obtained some large transparent crystals of MgO from the Norton Company. These are nominally undoped, but are found to contain a few chromium ions per million Mg^{2+} ions. We cut a rectangular prism from the most strain-free part of such a crystal for this investigation.

The R line fluoresced weakly but the line had a narrow width of 0.23 cm^{-1} at 4°K. Figure 2 shows a trace of the line. Once again the hump on the long-wavelength side would appear to be due to the Cr^{50} isotope. 4.3% of the intensity is subtracted off here, and what remains on the long-wavelength side of the peak is due only to Cr^{52}. Since the Cr^{50} line is symmetric, the asymmetry on the short-wavelength side can now be separated. Its intensity is just what is expected from Cr^{53} and Cr^{54} in their natural abundance. Such an analysis is indicated on Fig. 2.

[11] American Institute of Physics Handbook (McGraw-Hill Book Company, Inc., New York, 1963), pp. 8–7.
[12] D. F. Nelson and J. P. Remeika, J. Appl. Phys. 35, 522 (1964).

For ruby the measured value of the isotope shift is 0.13 cm^{-1} per mass unit, and for MgO:Cr^{3+} it is 0.17 cm^{-1} per mass unit. In both cases the lighter isotope lines are shifted to the red. The pair lines of ruby also exhibit isotope shift of roughly the same value. The lines from noncubic chromium sites in MgO are not sharp enough, in any available samples, to permit resolution of the isotope shift.

THEORETICAL

We attribute an isotope shift to the following process. The mean-square displacement of the impurity ion due to the lattice vibrations is different from that of the regular ions. The extent of the impurity-ion displacement depends on its mass; the smaller the impurity mass the larger its displacement. This quantity, then, is different for the various isotopes. Because of the electron-phonon interaction the energy levels of the ion, and hence, the frequencies, shift by an amount which depends on this mean-square displacement. The lines from the various isotopes, then, are shifted relative to each other. We calculate this isotope shift for the R lines of chromium in ruby and MgO.

We first derive an expression for the line shift due to the electron-phonon interaction. This consists of two parts. One is the line shift due to the thermal vibrations, that is, the vibrations which occur in addition to the zero-point vibrations and which vanish at absolute zero. This is the formula of McCumber and Sturge.[1] The second part is the shift due to the zero-point vibrations which is the only contribution at absolute zero.

On the basis of a simple model we derive an expression giving the dependence of the line shift on the mass of the impurity ion. This leads to an expression for the isotope shift.

Lattice vibrations also contribute to line broadening by a Raman process of phonon scattering.[1] This may obscure the isotope shift at finite temperatures. The
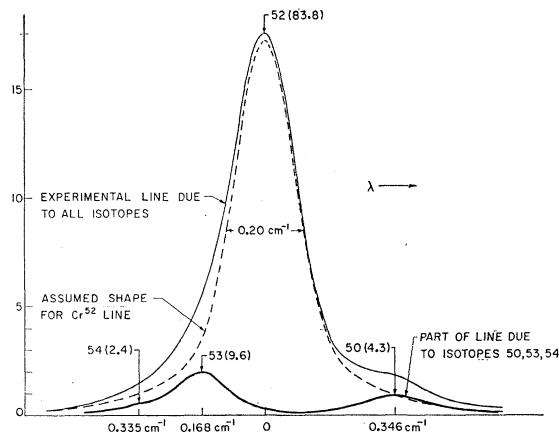

FIG. 2. Outline of the R line of MgO:Cr^{3+} showing its analysis into individual isotope components.

zero-point vibrations cannot contribute to this broadening mechanism, although they can cause a line shift, and hence, an isotope shift. We look for this isotope shift, then, at extremely low temperatures where the linewidth is smallest, and is caused only by the strains in the crystal. The line-shift situation at absolute zero is schematically represented on Fig. 3. The dashed line shows the position of all the isotope lines if zero-point vibrations did not exist. The zero-point vibrations, however, cause a shift which varies from isotope to isotope and this is represented on the figure.

A. Line Shift Due to Lattice Vibrations

We describe[1,3,13] the interaction between the impurity ion and the perturbed lattice by

$$\mathfrak{K}' = C\epsilon + D\epsilon^2, \qquad (1)$$

where C and D are linear and quadratic coupling parameters, respectively, and are functions of the lattice and electron coordinates. ϵ is the strain at the impurity, and we define it by

$$\epsilon = \delta u/d, \qquad (2)$$

where δu is the relative displacement of the ion from its equilibrium position between its neighbors. d is the interion distance. In reality, ϵ is a tensor of rank 2, and C and D are tensors of rank 2 and 4, respectively. However, to simplify calculations average values are understood and these quantities are expressed as scalars.

We restrict our considerations to the transition between the ^2E and $^4A_2$ levels of Cr^{3+} in ruby and MgO. The $^4A_2$ ground state is affected to a much smaller degree by the strains,[14] and we will only consider the effect of $\mathfrak{K}'$ on the ^2E level.

Under a static pressure, which introduces a small strain, the line shifts linearly with pressure and we get a static value for the linear parameter C, at the ^2E level. The values of this parameter for the R lines of ruby and $MgO:Cr^{3+}$ are almost identical.

When the strains are caused by lattice vibrations we also expect a line shift because of the interaction. We use the following expression for ϵ:

$$\epsilon = \partial u/\partial x \big|_{x=0}, \qquad (3)$$

where u is the amplitude of the lattice vibration. The energy shift due to the vibrations is calculated in the Appendix. Shifts cannot arise in first order from the term linear in ϵ. Shifts do come from the quadratic term in first order and from the linear term in second order. We find that the frequency shift may be written as the sum of two terms.

$$\Delta\omega = \Delta\omega(0) + \Delta\omega(T), \qquad (4)$$

[13] R. J. Adler, Bull. Am. Phys. Soc. **7**, 600 (1962).
[14] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).
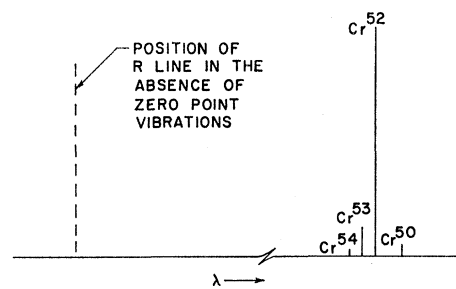

FIG. 3. Schematic representation of the shift due to the zero-point vibrations of the R lines of the individual chromium isotopes.

where

$$\Delta\omega(0) = -\sum_k \frac{1}{2Mv^2} \frac{|\langle^2E|C|^2E\rangle|^2}{\hbar} - \sum_k \frac{1}{2Mv^2}$$

$$\times \left[\langle^2E|D|^2E\rangle + \sum_j \frac{|\langle^2E|C|j\rangle|^2}{W(^2E)-W(j)} \right]\omega_k \quad (5)$$

is the shift due to the zero-point vibrations, and

$$\Delta\omega(T) = -\sum_k \frac{1}{2Mv^2} \left[\langle^2E|D|^2E\rangle + \sum_j \frac{|\langle^2E|C|j\rangle|^2}{W(^2E)-W(j)} \right]$$

$$\times 2\omega_k \left(\frac{1}{\exp(\hbar\omega_k/kT)-1} \right) \quad (6)$$

is the shift due to the thermal vibrations.[1] In Eqs. (5) and (6), k denotes available vibrational modes, M denotes the mass of the crystal, v is the average phonon velocity, and $|j$ denotes energy levels other than ^2E.

If we assume that the matrix elements above are independent of frequency, we expect, from Eq. (6), a shift $\Delta\omega(T)$ proportional to the total heat content of the crystal. That this is experimentally found justifies this assumption to some extent.[1–3] Inserting the static value of the linear coupling parameter instead of $\langle^2E|C|j\rangle$ in Eq. (6) we find that this linear parameter term is much too small to account satisfactorily for the experimental shift with temperature. We conclude that the D terms dominate in Eqs. (5) and (6) and these expressions reduce to

$$\Delta\omega(0) = -\frac{1}{Mv^2}\langle^2E|D|^2E\rangle \sum_k \frac{\omega_k}{2} \qquad (7)$$

and

$$\Delta\omega(T) = -\frac{1}{Mv^2}\langle^2E|D|^2E\rangle \sum_k \frac{\omega_k}{\exp(\hbar\omega/kT)-1}. \qquad (8)$$

If we reason in a purely classical manner, from Eqs. (1) and (2), we expect that in first order the terms linear in ϵ will average out due to the periodic nature of

the vibrations, and the shift becomes

$$\Delta\omega = \frac{D}{\hbar}\langle\epsilon^2\rangle = \frac{D}{\hbar}\frac{\langle\delta u^2\rangle}{d^2},\qquad(9)$$

that is, it is proportional to the mean-square strain or the mean-square relative displacement. This is precisely what our quantum-mechanical calculations have indicated. $\Delta\omega$ in Eqs. (7) and (8) can be written

$$\Delta\omega(0) = \frac{D}{\hbar}\langle\epsilon^2\rangle_0 = \frac{D}{\hbar}\frac{\langle\delta u^2\rangle_0}{d^2},\qquad(7')$$

and similarly, we get

$$\Delta\omega(T) = \frac{D}{\hbar}\langle\epsilon^2\rangle_T = \frac{D}{\hbar}\frac{\langle\delta u^2\rangle_T}{d^2},\qquad(8')$$

where $\langle\epsilon^2\rangle_0$ and $\langle\epsilon^2\rangle_T$ are quantum mechanical expressions for the strain due to the zero-point vibrations and to the thermal phonons, respectively. Now, if $\langle\delta u^2\rangle_T/d^2$ or $\langle\epsilon^2\rangle_T$ is calculated on the basis of a Debye model for ruby, with an effective Debye temperature of 760°K, then Eq. (8′) is in excellent agreement with theory.[1] A similar result is obtained for MgO:Cr^{3+} if an effective Debye temperature of around 700°K is used.[3] Combining Eqs. (7′) and (8′), we have

$$\Delta\omega(0) = \Delta\omega(T)(\langle\epsilon^2\rangle_0/\langle\epsilon^2\rangle_T).\qquad(10)$$

At $T = 100°$K, the thermal shifts, $\Delta\omega(T)$, found experimentally for the R lines of ruby and MgO:Cr^{3+} are -0.7 and -0.9 cm^{-1}, respectively.[1,3] $\langle\epsilon^2\rangle_{T=100}$ is calculated on the basis of the Debye model, and $\langle\epsilon^2\rangle_0$, the strain due to the zero-point vibrations, is calculated with the same model. From these quantities we can evaluate $\Delta\omega(0)$. A zero-point shift of -45 cm^{-1} is obtained for the R line of MgO:Cr^{3+}, with an almost identical value for ruby.

B. Vibrations of an Impurity Ion in a Host Lattice

We must now consider how the impurity ion vibrates in the host lattice. In general, the modes of vibration are modified and these modifications are greatest in the vicinity of the impurity. This is not a simple problem to treat. Numerical calculations of the mean-square displacement of the impurity ion have been carried out by a number of investigators.[9,15] It appears that this displacement is not very dependent on the properties of the host lattice.

Of particular relevance is the calculation of Lipkin.[16] He showed that, at zero temperature, the mean-square

displacement $\langle u'^2\rangle_0$ of an impurity ion of mass m' in a crystal whose regular ions have mass m, is given to a very good approximation by the mean-square displacement of the ion of mass m' in the "equivalent heavy lattice." By "equivalent heavy lattice" is meant a lattice identical with the original in every way except that all the ions have mass m'.

We wish to calculate the ratio $\langle u'^2\rangle_0/\langle u^2\rangle_0$, where $\langle u^2\rangle_0$ is the zero-temperature mean-square displacement of the regular ions of mass m in the host crystal away from the impurity, and $\langle u'^2\rangle_0$ is the mean-square displacement of the impurity ion in this crystal. We calculate $\langle u^2\rangle_0$ by assuming that the vibrations of the regular ion are unaffected by the impurity, and we calculate $\langle u'^2\rangle_0$ by considering the "equivalent heavy crystal."

At zero temperature, the zero-point vibration occurs in every mode of the original crystal and of the equivalent heavy crystal. The same modes in $\mathbf{k}$ space are available for both crystals, but their frequencies are different. For the same $\mathbf{k}$ value the frequencies are in the ratio of the inverse square root of the masses, i.e.,

$$\omega_k'/\omega_k = (m/m')^{1/2}.\qquad(11)$$

The displacement of m due to the zero-point vibration in the kth mode is

$$u_0(\mathbf{k}) = (\hbar/Nm\omega_k)^{1/2}\sin(\mathbf{k}\cdot\mathbf{x} - \omega t),\qquad(12)$$

hence

$$\langle u^2(\mathbf{k})\rangle_0 = \hbar/2Nm\omega_k.\qquad(13)$$

Similarly, for the ion of mass m' in the second crystal $\langle u'^2(\mathbf{k})\rangle_0 = \hbar/2Nm'\omega_k'$, where N is the number of ions in both crystals.

For every allowed value of $\mathbf{k}$ we have

$$\frac{\langle u'^2(\mathbf{k})\rangle_0}{\langle u^2(\mathbf{k})\rangle_0} = \frac{m\omega_k}{m'\omega_k'} = \left(\frac{m}{m'}\right)^{1/2}.$$

Summing over all $\mathbf{k}$ values gives

$$\langle u'^2\rangle_0/\langle u^2\rangle_0 = (m/m')^{1/2}.\qquad(14)$$

The detailed calculations of Dawber and Elliott[15] for an impurity ion in a simple cubic crystal confirms that this result is a very good approximation.

For chromium in ruby and MgO, we will assume that this mass dependence is obeyed although we no longer have the simple case of an impurity in a monatomic lattice. We will take the ratio of $m/m' = \frac{2}{5}$.[17]

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[15] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) A273, 222 (1963).

[16] H. J. Lipkin, Ann. Phys. (N. Y.) 23, 28 (1963).

[17] For MgO the masses are 24 (Mg) and 16 (O). The most abundant chromium isotope has a mass of 52. A mass ratio of $m/m' = \frac{2}{5}$ is then an appropriate value to adopt for MgO:Cr^{3+}. For Al$_2$O$_3$ the masses are 27 (Al) and 16 (O) so that the average mass is again around 20. The same mass ratio then seems appropriate for ruby.

C. Dependence of Zero-Temperature Shift on Impurity Mass

The quantity we are concerned with is the mean-square *relative* displacement: $\langle \delta u^2 \rangle_0$. The optical phonons are much more effective than the acoustical phonons, and we adopt the following expression for $\langle \delta u^2 \rangle_0$. (See the simple linear model in Fig. 4.)

$$\langle \delta u^2 \rangle_0 = \alpha [\langle u'^2 \rangle_0 + \langle u^2 \rangle_0], \qquad (15)$$

where u' is the displacement of the chromium ion and u is the displacement of the neighboring host ion which is assumed for simplicity to have its unperturbed value. α is a factor of proportionality.

We can express Eq. (7′) as

$$\Delta\omega(0) = \beta [(\langle u'^2 \rangle + \langle u^2 \rangle)/d^2] = \frac{\beta}{d^2} \langle u^2 \rangle [1 + (m/m')^{1/2}]. \qquad (16)$$

This is the expression we need, it tells us how the zero-temperature shift varies with the mass m' of the impurity. It is represented schematically in Fig. 3. β is a factor of proportionality. For a small change in m', the shift is nearly linearly proportional to the change in m'. When m increases by unit mass, $\Delta\omega(0)$ varies as

$$\delta[\Delta\omega(0)] = -\frac{\Delta\omega(0)}{2m'} \left[\frac{(m/m')^{1/2}}{1 + (m/m')^{1/2}} \right]. \qquad (17)$$

The heavier the isotope the less its displacement and, consequently, the less is its zero-temperature shift. This is indicated in Eq. (17). For chromium in ruby and in MgO, we have $m/m' = \frac{2}{5}$ and $\Delta\omega(0) = -45$ cm^{-1}. Inserting these values in Eq. (17), we calculate an isotope shift of 0.18 cm^{-1} per unit mass. The experimentally determined values are 0.13 cm^{-1} for ruby and 0.17 cm^{-1} for MgO.

In applying the above arguments to the R line of MgO:Cr^{3+} we have neglected to take into account the change in force constant. This change is due to the chromium ion having a positive charge of three units while the ion it replaces has a charge of two units. The closeness of the experimental shifts for ruby and MgO:Cr^{3+} indicates that this change in force constant
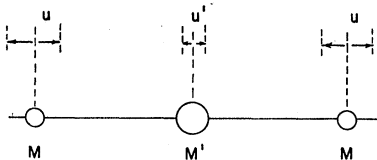
does not seem to alter materially the mass dependence, Eq. (14), used in the calculations.

CONCLUSION

In spite of the simplifying assumptions made in estimating the isotope shift, there is close agreement between experimental and calculated values. We conclude that the mass dependence in the amplitude of the impurity ion is capable of explaining the observed shifts. This experiment can be further thought of as a test of the "equivalent heavy lattice" model for calculating the mean-square amplitude of vibration summed over all frequencies for an impurity ion in a monatomic lattice. This does not in itself imply anything about the spectrum of the impurity vibrations. The analogy between the interaction of the ion with its vibrational state and the interaction of the electron with its own field is interesting and has been pointed out by Kiel.[18] In this respect, the origin of the isotope shift is a process parallel to that which produces the Lamb shift in atoms and ions.

APPENDIX

We use perturbation theory to calculate the additional energy of the $|^2D,n\rangle$ level due to the interaction $\mathfrak{IC}'$. The quantum number n denotes the vibrational state of the lattice. Using a second quantized expression for the amplitude of lattice vibrations u,[19] we find from Eq. (3) that

$$\epsilon = \sum_k \left(\frac{\hbar\omega_k}{2Mv^2} \right)^{1/2} (a_k - a_k^\dagger), \qquad (A1)$$

where $a_k^\dagger$ and a_k are phonon creation and destruction operators, respectively. M is the mass of the crystal, $\mathbf{k}$ denotes the vibrational mode, and v is the average phonon velocity.

Introducing Eq. (A1) into Eq. (1), we find that the term containing C is linear in a_k and $a_k^\dagger$, and can only contribute in second order. The term containing D can contribute in first order. The only nonzero contributions come from combinations of the type $a_k a_k^\dagger$ and $a_k^\dagger a_k$.

$$\langle \delta u^2 \rangle_0 = \alpha \left[\langle u'^2 \rangle_0 + \langle u^2 \rangle_0 \right]$$

FIG. 4. Simple linear model used to derive the expression for the mean-square relative displacement of the impurity ion.

[18] A. Kiel, Phys. Rev. **126**, 1292 (1962).
[19] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Eq. (33), Chap. 2.

The expression obtained for the energy shift is

$$\Delta W = -\sum_{k,j} \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(j)+\hbar\omega_k} \frac{\hbar\omega_k}{2Mv^2}\langle n|a_k a_k{}^\dagger|n\rangle$$

$$-\sum_{k,j} \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(j)-\hbar\omega_k} \frac{\hbar\omega_k}{2Mv^2}\langle n|a_k{}^\dagger a_k|n\rangle$$

$$-\sum_{k} \langle {}^2E|D|{}^2E\rangle \frac{\hbar\omega_k}{Mv^2}\langle n|a_k{}^\dagger a_k+\tfrac{1}{2}|n\rangle . \qquad (A2)$$

In Eq. (A2) j denotes all available electronic levels including the ${}^2E$ level.

When j denotes the ${}^2E$ level the contribution from the first two terms of Eq. (A2) becomes

$$-\sum_{k} \frac{|\langle {}^2E|C|{}^2E\rangle|^2}{2Mv^2}\langle n|a_k a_k{}^\dagger - a_k{}^\dagger a_k|n\rangle$$

$$=-\sum_{k} \frac{|\langle {}^2E|C|{}^2E\rangle|^2}{2Mv^2} . \qquad (A3)$$

When j denotes levels other than ${}^2E$, then for the case of chromium in MgO, we can assume that $|W({}^2E)-W(j)|\gg\hbar\omega_k$, and the contribution from the first two terms of Eq. (A2) becomes

$$-\sum_{k}\sum_{j}' \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(i)} \frac{\hbar\omega_k}{Mv^2}\langle n|a_k{}^\dagger a_k+\tfrac{1}{2}|n\rangle . \qquad (A4)$$

The prime in the j summation means that the $j\neq{}^2E$ in the summation.

In the case of ruby the ${}^2E$ level is split into two components whose separation is 29 cm^{-1}. In calculating the shift of any one of these two levels using Eq. (A2), the summation over j levels will have to include the other level 29 cm^{-1} away. This is within the range of phonon energies and resonant denominators will occur in the first two terms. For ruby, McCumber and Sturge[1] found that this contribution to ΔW is finite but negligible in

comparison with the remainder of the expression. We assume that all other levels are sufficiently far away so that $|W({}^2E)-W(j)|\gg\hbar\omega_k$. The line-shift calculations for ruby and MgO:Cr^{3+} are then identical. In both cases the energy shift of the $|{}^2E,n\rangle$ level is

$$\Delta W = -\sum_{k} \frac{|\langle {}^2E|C|{}^2E\rangle|^2}{2Mv^2} - \sum_{k}\left[\langle {}^2E|D|{}^2E\rangle \right.$$

$$\left. +\sum_{j}' \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(j)}\right]\frac{\hbar\omega_k}{Mv^2}\langle n|a_k{}^\dagger a_k+\tfrac{1}{2}|n\rangle . \quad (A5)$$

In this expression $a_k{}^\dagger a_k$ is the number operator, giving the number of thermal phonons, $n(\mathbf{k})$, in the kth mode:

$$n(\mathbf{k})=\frac{1}{\exp(\hbar\omega_k/kT)-1} .$$

The part of Eq. (A5) containing $a_k{}^\dagger a_k$ gives a temperature-dependent energy shift $\Delta W(T)$, which vanishes when $T=0°$K. The remaining part of Eq. (A5) is the contribution of the zero-point vibrations to the energy shift $\Delta W(0)$. These two contributions are

$$\Delta W(0)=-\sum_{k} \frac{|\langle {}^2E|C|{}^2E\rangle|^2}{2Mv^2} - \sum_{j}\left[\langle {}^2E|D|{}^2E\rangle \right.$$

$$\left. +\sum_{j}' \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(j)}\right]\frac{\hbar\omega_k}{2Mv^2}, \quad (A6)$$

and

$$\Delta W(T)=-\sum_{k}\left[\langle {}^2E|D|{}^2E\rangle \right.$$

$$\left. +\sum_{j}' \frac{|\langle {}^2E|C|j\rangle|^2}{W({}^2E)-W(j)}\right]\frac{\hbar}{Mv^2}\frac{\omega_k}{\exp(\hbar\omega_k/kT)-1} . \quad (A7)$$

These lead directly to Eqs. (5) and (6) for the zero-point and temperature-dependent frequency shifts.