Zero-Point Phonon Contribution to the Hyperfine Coupling of S-State Ions*

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The temperature-independent phonon zero-point motion is shown to decrease the hyperfine coupling constant A for Mn^{2+} ions in a cubic environment. A spherical approximation is made for the phonon vibrational modes appropriate to a rocksalt structure, enabling the inclusion of contributions from both the acoustic and optical branches. Numerical calculations are performed for vibrational parameters appropriate to both MgO and SrO. The temperature-dependent part of the decrease in A due to thermal phonon excitation is also evaluated for both hosts. Comparing the two calculations, the temperature can be determined at which the decrease in A due to thermal excitations equals the decrease due to zero-point excitations. These temperatures are 383°K for MgO and 133°K for SrO. Use is then made of the observed decrease in A with temperature to find the magnitude of the zero-point reduction in both hosts. We find $\Delta A_{Z.P.}(\text{MgO}:Mn^{2+}) \cong -0.8 \times 10^{-4}$ cm^{-1} and $\Delta A_{Z.P.}(\text{SrO}:Mn^{2+}) \cong -1.4 \times 10^{-4}$ cm^{-1}. The change in A, $\Delta A_{Z.P.}/[\Delta A (T=0) + \Delta A_{Z.P.}]$, due to phonon zero-point motion is therefore 0.97% for MgO:Mn^{2+} and 1.70% for SrO:Mn^{2+}, and the $T=0$ "rigid-lattice" values are estimated to be -82.3×10^{-4} cm^{-1} for both hosts.

I. INTRODUCTION

A PREVIOUS calculation[1] of the temperature dependence of the hyperfine coupling for Mn^{2+} in MgO demonstrated that the thermal excitation of phonons was responsible for the observed decrease in A^{55} with increasing temperature. A point-charge calculation carried out in that paper yielded a coupling constant eight times too small when compared with the results of Walsh et al.[2] A subsequent letter by Šimánek and Huang[3] took into account the effect of covalency, in particular the polarization of the inner ns shells of the Mn^{2+} ion by the spin-polarized deformed d-electron molecular orbitals. In this paper, we shall examine the effect of zero-point phonon motion on the hyperfine coupling constant for Mn^{2+} in MgO and SrO. The connection between the thermal decrease in A and the associated zero-point decrease is clear. However, the lack of a Bose weighting factor severely complicates the estimate of the zero-point decrease since the entirety of the lattice vibrational modes contribute, even at low temperatures.

Because of the difficulties associated with the precise value of the coupling constant and, more importantly, the difficulty with the lattice vibrational spectrum of the hosts, we shall introduce a "model" lattice vibrational spectrum. This model will enable us to compute both the thermal and zero-point decrease in the hyperfine coupling constant. The temperature at which the thermal decrease in the hyperfine field equals the (temperature-independent) zero-point decrease can then be determined. It will turn out that this temperature is relatively insensitive to the specific model, as indicated from its small variation when large changes are made in the model parameters. A fit is then made of the calculated temperature-dependent part of the decrease in hyperfine field to the observed temperature-dependent decrease. This allows the zero-point contribution to be "read off" the experimental curve by simply finding the experimental decrease in A at *that temperature* at which the model calculation indicates the zero-point reduction equals the thermal reduction. This technique should provide for a relatively accurate estimate of the zero-point reduction in the hyperfine field. In the next section, the model for the lattice is described, and in Sec. III the calculations are carried out for two isomorphic host lattices, MgO and SrO. These two represent rather extreme cases, the former being quite hard, the latter rather soft in its elastic properties. Recent temperature-dependence measurements of the hyperfine field of SrO:Mn^{2+} by Rosenthal et al.,[4] together with the measurements of Walsh et al.[2] on Mn^{2+} in MgO, allow us to find explicit values for the zero-point decrease of $A^{55}(Mn^{2+})$ in both these hosts. Though the lattice model used for these
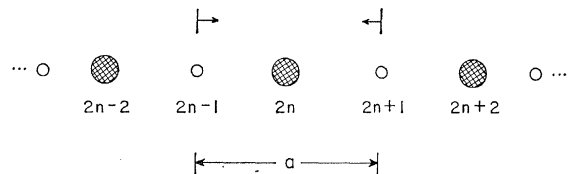

Fig. 1. A schematic of the diatomic linear chain used as a model of the MgO and SrO lattices in this paper. The small circles represent the (lighter) oxygen anions, the large shaded circles the (heavier) cations. The mode Q in which we are interested is simply $x_{2n-1} - x_{2n+1}$, where x_n is the displacement of the nth ion parallel to the length of the chain.

¹ E. Šimánek and R. Orbach, Phys. Rev. **145**, 191 (1966).
² W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965).
³ E. Šimánek and Nai Li Huang, Phys. Rev. Letters **17**, 134 (1966).
⁴ J. Rosenthal, L. Yarmus, and R. H. Bartram, Phys. Rev. **153**, 407 (1967). We are indebted to Dr. Rosenthal for sending us a copy of this paper prior to publication.

materials is admittedly crude, an observed relative insensitivity to changes in model parameters of our technique gives us some confidence in our results. Clearly, when proper lattice eigenvectors and eigenvalues are available for these hosts, a much more reliable job can be done. In the absence of such information, one must unfortunately resort to the "model-lattice" technique used here.

II. FORMULATION OF THE COUPLING TO THE "MODEL LATTICE"

Our previous computation[1] of the temperature dependence of the hyperfine field relied on a Debye model for the lattice vibrations. This led to the result

$$A(T) = A(T=0)\left[1 - CT^4 \int_0^{\Theta/T} (x^3 dx/(e^x - 1))\right]. \quad (1)$$

The coefficient C was estimated in that paper from a point-charge model, with the effects of covalency introduced in a subsequent paper[3] by one of us (E.S.) and Nai Li Huang. The complexity of the lattice vibrational spectrum makes the determination of C in (1) almost academic, since so much error can result from the use of a Debye approximation. Thus, we shall first examine a lattice for which the eigenvectors and eigenvalues can be found analytically, the diatomic linear chain. Consider a chain composed of cations and anions of mass M and m, respectively, coupled with a force constant μ. For simplicity, we consider longitudinal vibrations only. The local vibrational mode Q which gives rise to s-like admixtures to the $3d$ electronic states is then of the type pictured[5] in Fig. 1. Using running waves, this vibration Q can be written as

$$Q = 2iA e^{ikna} \sin(ka/2), \quad (2)$$

where a is the static anion-anion distance, and A is the plane-wave amplitude for anion motion. The eigenfrequencies of this lattice are given by

$$\omega^2 = \frac{\mu}{mM}[M + m \mp (M^2 + m^2 + 2Mm\cos(ka))^{1/2}], \quad (3)$$

where the upper sign refers to the acoustic branch, the lower to the optical branch. The eigenvectors are found from the equations

$$mA^2 + MB^2 = m + M,$$

$$\frac{A}{B} = \frac{2M\cos(ka/2)}{M - m \pm [M^2 + m^2 + 2Mm\cos(ka)]^{1/2}}, \quad (4)$$

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[5] This mode is appropriate to longitudinal vibrations in a linear chain. Clearly, all the other vibrations of an octahedron of oxygens in MgO and SrO also contribute (see Ref. 1). We have considered only this particular term for convenience. We shall eventually derive a *ratio* for the thermal and zero-point reductions of A, so that the absence of the other modes is not serious. We are not pretending to derive an absolute estimate of the change in hyperfine field in this paper.

where B is the plane-wave amplitude for cation motion. Using (2) and (4), the amplitude of Q can be determined for arbitrary k in either branch. It is interesting to note that, at $k = \pm \pi/a$, $A = 0$ in the acoustic branch, but $A = [(m+M)/m]^{1/2}$ in the optical branch. This means that the primary contribution to the phonon-induced change in hyperfine field at large k values comes from the contribution of the optical branch. Because the Debye spectrum is supposed to mirror only the behavior of the acoustic branch, one should thus have grave doubts about using the Debye approximation at high temperatures.

The next step is the computation of $\langle Q^2 \rangle$, the quantity responsible[1] for the phonon-induced decrease in the hyperfine constant A. It is tempting to simply compute this quantity for the one-dimensional lattice. We shall not carry out this computation because of the well-known peculiarities of the density of states in one dimension, as compared to three. Rather, we shall make a spherical approximation, assuming that (2), (3), and (4) are appropriate for running waves in three dimensions. We are quite aware of the crudity of this approximation, but we believe it to represent a significant advance over a Debye model. We will find the "correct" behavior at the center of the zone and near the zone boundary for some directions of **k**. Performing this "spherical" approximation, and writing the interaction Hamiltonian as $\mathcal{H}' = V_{0L}(Q/a)$, where V_{0L} is an orbital operator with the units of energy, we find

$$\langle \mathcal{H}'^2 \rangle = \frac{V_{0L}^2}{a^5} \frac{\hbar}{\pi^2 \rho}$$

$$\times \int_0^\pi \frac{y^2 \sin^2(y/2) A^2(y)}{\omega(y)} \{n[\omega(y)] + \tfrac{1}{2}\} dy, \quad (5)$$

where y is the dimensionless parameter ka, and $n[\omega(y)]$ is the Bose factor $\{\exp[\hbar\omega(y)/k_B T] - 1\}^{-1}$.

III. EVALUATION AND DISCUSSION OF NUMERICAL RESULTS FOR MgO AND SrO

Equation (5) must be evaluated numerically for values of $\omega(y)$ and $A(y)$ as determined by (3) and (4), respectively. It is first necessary, however, to fit (3) and (4) to the host lattice in question. We choose to fit our spherical model to the isomorphic lattices MgO and SrO. For the former, we are able to make use of the Raman data of Mon[6] which give the vibrational fre-

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[6] J. P. Mon, J. Phys. (Paris) **26**, 611 (1965). [*Note added in proof.* During the course of their search for the Raman spectrum of MgO, R. M. Macfarlane and M. J. Weber (private communication) discovered that the spectrum reported by J. P. Mon was not a Raman spectrum, but rather the one-phonon sidebands of trivalent chromium impurities in his MgO sample. This discovery casts doubt upon the accuracy of our model lattice vibrational spectrum. We do believe, however, that the frequencies we used were not very far from the true MgO vibrational frequencies, and thus that our numerical estimates are not seriously in error.]

quencies at the Γ, X, and L points of the MgO zone. We use the masses of Mg and O, and then adjust the force constant to give something like the average of the vibrational frequencies at these critical points. Extrapolation to zero wave vector of the resulting dispersion law results in a velocity of sound equal to 8.6×10^5 cm/sec, very close to the observed[7] longitudinal phonon velocity of 9.1×10^5 cm/sec.

The integrations in (5) were carried out numerically for the temperature-dependent and -independent parts. The contribution of the acoustic and optical branches to the integral were separated from one another. As expected, the former contributed the majority of the temperature-dependent contribution at low temperatures. The optical branch, for lattice vibrational parameters appropriate to MgO, gave comparable temperature-dependent contributions near 350°K. At 1000°K, the contribution from the optical branch exceeded that from the acoustic branch by nearly 30%. The results for the temperature-independent (zero-point) contributions were even more striking. The optical branch contributed more than twice that of the acoustic branch. We believe this is due in large part to the behavior of the lattice vibrations near the zone boundary where the density of states is greatest. The eigenvectors of the acoustic branch at $k = \pi/a$ are appropriate to opposing motion of only the heavier (cation) neighboring ions, while the optical branch eigenvectors correspond to the opposing motion of only the lighter (anion) neighboring ions. The former motion has no projection on Q, while the latter, in fact, directly represents the vibration Q. Hence, the optical branch near $k = \pi/a$ is contributing much more to the decrease of A than the acoustic branch in the same region. The high density of states in this region then gives even further weight to the optical phonon contribution to the zero-point phonon decrease of A. Putting all these contributions together, it was found, for the lattice vibrational parameters appropriate to MgO, that the zero-point decrease in $A(T)$ equaled the temperature-dependent decrease at $T = 383°K$. Using the curve for $A(T)$ in Walsh et al.[2] at that temperature, we find $A(383°K) = -80.7 \times 10^{-4}$ cm^{-1}. The $T = 0$ value[2] equals -81.5×10^{-4} cm^{-1}, so that we are able to estimate

$$\Delta A_{\text{Z.P.}}^{\text{MgO}} = -0.8 \times 10^{-4} \text{ cm}^{-1}. \qquad (6)$$

This result is of some importance because it represents a 0.97% reduction in the hyperfine field from that value appropriate to a "rigid" MgO lattice. Clearly, one must consider this decrease explicitly when attempting to arrive at the systematics of A for the same cation in a variety of host materials.

To demonstrate this point, we consider next the rather extreme case of SrO:Mn^{2+}, which was recently examined by Rosenthal et al.[4] for temperatures ranging

from 77 to above 1000°K. Unfortunately, our analysis, which requires an effective force constant for SrO, is hindered because even the velocity of sound is unknown for this material. We therefore used the correct values for the Sr^{++} and O$^=$ masses and adjusted the force constant μ so as to obtain the observed[4] temperature dependence of $A(T)$ in SrO. We found that we must reduce μ by a factor of 7.9 from that used in our model of MgO to roughly fit the curve of Rosenthal et al. for SrO:Mn^{2+}. This corresponds to a zone-boundary acoustic phonon energy of 75°K and an acoustic velocity of 3×10^5 cm/sec. It seems to us that these figures are not completely unrealistic for this host material, primarily because of its "soft" mechanical properties. In any case, with this assumption, the thermal decrease in $A(T)$ is found to equal the zero-point decrease at $T = 133°K$. The data of Rosenthal et al.[4] indicate that $A(133°K) = -79.6 \times 10^{-4}$ cm^{-1}. The $T = 0$ value[8] equals -80.9×10^{-4} cm^{-1}, so that we estimate

$$\Delta A_{\text{Z.P.}}^{\text{SrO}} = -1.3 \times 10^{-4} \text{ cm}^{-1},$$

or about a 1.7% decrease from the "rigid-lattice" value. This result is, unfortunately, rather suspect because of the lack of pressure data on SrO:Mn^{2+} which would enable us to include the effects of lattice dilatation. By leaving out this correction we have, in fact, underestimated the temperature-dependent decrease of A if SrO behaves in a manner similar to MgO. Walsh et al.[2] have found A to increase (negatively) with increasing lattice volume so that the measured thermal decrease of A actually includes an increase of A due to lattice dilatation. When account is made of this correction, a greater value of the thermal decrease is obtained. We can make a rather crude estimate of this effect by scaling the effect of thermal expansion of MgO to SrO. We are interested in $A^{\text{SrO}}(T)$ at 133°K. We multiply this temperature by the ratio of the Debye temperatures for MgO and SrO, the latter $\sim 210°K$ from the value we obtained for the velocity of sound. This scaling results in an MgO "equivalent" temperature of 470°K. Reference to Walsh's curve for the effect of thermal expansion on A in MgO shows a 0.1×10^{-4} cm^{-1} increase at that temperature. Hence, we add this correction to our previous value $\Delta A_{\text{Z.P.}}^{\text{SrO}}$ and obtain

$\Delta A_{\text{A.P.}}^{\text{SrO}}$(with lattice expansion)

$$= -1.4 \times 10^{-4} \text{ cm}^{-1}.$$

We shall use this result in our subsequent discussion.

If we add the zero-point values for A to the $T = 0$ values, we obtain the following rigid-lattice values:

$$A_{\text{R.L.}}^{\text{MgO}} \equiv \Delta A_{\text{Z.P.}}^{\text{MgO}} + A^{\text{MgO}}(T = 0)$$
$$= -82.3 \times 10^{-4} \text{ cm}^{-1},$$

$$A_{\text{R.L.}}^{\text{SrO}} \equiv \Delta A_{\text{Z.P.}}^{\text{SrO}} + A^{\text{SrO}}(T = 0)$$
$$= -82.3 \times 10^{-4} \text{ cm}^{-1}.$$

[7] H. B. Huntington, Solid State Phys. 7, 214 (1958).

[8] A. J. Shuskis, Jr., J. Chem. Phys. 41, 1885 (1964).

It is rather interesting that these values are identical. A simple covalency argument would suggest that $A_{\text{R.L.}}^{\text{SrO}} > A_{\text{R.L.}}^{\text{MgO}}$, because the larger lattice constant of SrO would mean a smaller normalization correction for the $3d$ wave function. The near equality of the two rigid-lattice values for A makes this argument suspect.

It also adds tentative weight to an argument[9] that the "instability" of the O^{2-} wave function is responsible for this consistency. It is well known[10] that the "size" of the O^{2-} wave function is determined by the potential well in which it sits. Increasing the metal-oxygen distance may thus result in an increase in the O^{2-} wave function which would cause the covalency to remain relatively constant. This argument is not necessarily weakened by the fact that the cubic field splitting a varies from 18.6×10^{-4} cm^{-1} for MgO:Mn^{2+}[11] to $<1 \times 10^{-4}$ cm^{-1} for SrO:Mn^{2+},[12] because a is proportional only to the difference in π and σ bonding. It might well be the case that small changes in π and σ bonding, combined with a reduction in the point-charge contribution because of the larger lattice constant, are

responsible for the differences in a between MgO and SrO. To check this, one should note that Walsh[13] finds $(\ln\Delta A/\ln\Delta V)_T = 0.06$, whereas $(\ln\Delta a/\ln\Delta V)_T = -7.08$ for Mn^{2+} in MgO. It is clear that the latter quantity changes with volume much more rapidly than the former. If we extrapolate Walsh's result for the pressure dependence of a to that volume for which $a \sim 0$, appropriate to SrO:Mn^{2+}, we find that A at the same volume would have been increased by only 0.8 cm^{-1}. Too much attention should not be paid to this extrapolation because of the obvious problem of linearity of A and a over such a large change in volume. Nevertheless, it is clear that a is much more sensitive to volume than A, so that one should not attempt to use large changes in a to rule out an apparent constancy of A.

Finally, we should like to emphasize again that the results we have presented here are only an approximation to the truth. One should use, instead of an elementary linear chain model, the correct eigenvectors and eigenvalues appropriate to MgO and SrO in order to correctly determine $A(T)$ and $\Delta A_{\text{z.p.}}$. We have resorted to this very approximate calculation only to give a physical picture of the zero-point reduction of the hyperfine coupling constant A for an S-state ion in a dielectric host.

[9] E. Šimánek, Nai Li Huang, and R. Orbach, J. Appl. Phys. (to be published).

[10] Y. Yamashita and M. Kojima, J. Phys. Soc. (Japan) **7**, 261 (1952); R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[11] W. Low, Phys. Rev. **105**, 793 (1957).

[12] W. Low, Phys. Letters **11**, 115 (1964).

[13] W. M. Walsh, Jr., Phys. Rev. **122**, 762 (1961).