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Temperature-Dependent Spin-Hamiltonian Parameters of Mn^{2+} in Trigonal Sites of $CaCO_3$ †

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The spin-Hamiltonian parameters of divalent manganese in $CaCO_3$ have been measured over the temperature range 4.2–850 °K using electron-spin-resonance-absorption techniques. Eigenvalues to the spin-Hamiltonian and best-fit parameters were obtained using perturbation calculations, where the off-diagonal component in the hyperfine interaction is treated as the major perturbation. The crystalline-field parameters and the hyperfine-coupling constant A were found to decrease in magnitude with increasing temperature, although there was no measurable variation of the g value over this temperature range. Variation in the parameters with temperature is discussed in terms of implicit (thermal-expansion) and explicit (lattice-vibration) effects. Contributions from implicit effects were evaluated using previously reported isothermal pressure-dependent data. After correcting the experimental data for the implicit effect, a large residual-temperature variation is found for the crystalline-field parameters D and a_0. This residual-temperature variation is attributed to lattice vibrations which couple into the crystalline-field splitting energy. Temperature variations in the axial crystalline-field-splitting energy can be explained, in part, by resonant vibrations which couple to the impurity ion via a relativistic second-order correction proposed by Wybourne. Temperature variations in the hyperfine-coupling constant A are also due primarily to explicit effects. A detailed theoretical analysis of the temperature dependence of A for Mn^{2+} in a noncubic environment has not been carried out. However, it is possible to qualitatively interpret this temperature variation if it assumed that a large-amplitude local-mode vibration couples strongly to the hyperfine-coupling parameter.

I. INTRODUCTION

In the past there has been a great deal of interest in the origin of crystal-field-splitting energies of S-state ions in various crystalline environments. Several mechanisms have been proposed to explain the manner in which the spin degeneracy of an S-state ion is lifted by the presence of a crystalline electric field.[1–11] In general, the crystal-field-splitting energy arises from mechanisms involving second- or higher-order perturbation terms in the spin-orbit, spin-spin, and crystal-field interactions. There has been some success in determining the most important contributions to the crystal-field-splitting energies for Mn^{2+} in ZnF_2 and MnF_2; however, it is not clear that the same mechanisms are predominant in other environments.[9–11] Recently, Wybourne showed that if relativistic radial wave functions are used in the crystal-field calculations, there would be an important second-order contribution to the ground-state splitting of rare-earth S-state ions.[12] Van Heuvelen extended these calculations to the Mn^{2+} ion and concluded that the relativistic contribution to the axial crystalline-field splitting D predicts the correct sign but about one-half the magnitude of D in a number of salts.[13] The relativistic contribution to the crystal-field-splitting parameters was shown to be important in the case of Mn^{2+} in NaCl.[14]

Another property of S-state ions which has been given a great deal of attention is the origin of the hyperfine interaction and the observed decrease of the hyperfine-coupling constant with increasing temperature in cubic environments.[15–29] Walsh, Jeener, and Bloembergen first recognized that the hyperfine-coupling temperature dependence $A(T)$ for Mn^{2+} in cubic environments is largely due to explicit effects, e.g., lattice vibrations.[15] However, as these investigators have pointed out, the implicit (thermal-expansion) effect also contributes to the variation of the hyperfine-coupling constant with temperature. In the case of Mn^{2+} in MgO, the implicit effect is small compared to the explicit effect. Simanek and Orbach proposed that the explicit temperature dependence of A for S-state ions in cubic environments is due to the mixing of the Mn^{2+} $3d$ orbitals with higher-lying ns orbitals through the orbit-lattice interaction.[16] This treatment was later extended to Mn^{2+} and Eu^{2+} in the eightfold coordinated cubic environment of the alkaline-earth flourides.[20-28] Although these descriptions of the hyperfine-coupling temperature dependence are functionally correct, there is a discrepancy between theoretical and experimental parameters involved in the analysis. This discrepancy generally increases with increasing host-lattice cation radius.[21–25] In the case of Mn^{2+} in MgO, part of the discrepancy has been attributed to covalency effects.[17] A generalized theory which includes lattice vibrations over the entire phonon spectrum has not accounted for the discrepancies; however, such calculations show that optical phonons contribute significantly to both the thermal and rigid-lattice values of the hyperfine-coupling constant.[22,28] These results suggest either that the point-charge lattice continuum model is insufficient in treating the hyperfine-coupling temperature dependence or that some other mechanism is operative in this situation.

This paper presents the results of an investigation on the temperature dependence of the crystal-field-splitting parameters and hyperfine-coupling constant of Mn^{2+} in single-crystal calcite, $CaCO_3$. This investigation was conducted for several reasons. First, the implicit contributions to the temperature-dependent data can be evaluated from hydrostatic-pressure studies by Wait on this system.[29] In most situations these contributions are neglected, since pressure data are seldom available. Second, there is an inherent interest in relative sizes of the implicit and explicit contributions to the spin-Hamiltonian parameters, and the specific nature of the explicit effects. In addition, contributions to the temperature variations of the crystal-field parameters from explicit effects could provide information on the predominant mechanisms giving rise to the crystal-field parameters. Finally, although there is an abundance of data available on hyperfine-coupling temperature dependence for *S*-state ions in cubic environments, there is an obvious lack of experimental and theoretical information for *S*-state ions in noncubic environments.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The electron-spin-resonance-absorption data were taken with a conventional 3-cm-wavelength spectrometer utilizing superheterodyne detection for low-temperature measurements and homodyne detection for the high-temperature measurements. All low-temperature data were obtained using a cylindrical cavity resonator operating in the TE_{011} mode, while the data above room temperature were taken with a half-wavelength rectangular cavity enclosed in a cylindrical oven similar to that described by Walsh *et al.*[15] The high-temperature measurements were taken in such a manner that temperature fluctuations no greater than 2 °K occurred during a run, corresponding to a cavity frequency drift which was less than 0.1 MHz. Zeeman field strengths were measured with a proton-resonance magnetometer, and audio modulation was used throughout the experiment. Both the magnetometer and microwave frequencies were monitored with the same electronic counter.

Oriented calcite single crystals used in this investigation were cut from natural rhombohedral samples obtained from the Karl Lambrecht Corp., Chicago, Ill. These samples contained manganese concentrations of the order of a few hundred parts per million giving linewidths of a few oersteds. The parameters were evaluated from data taken with the external field oriented along the calcite [111] axis, where most transitions are well resolved. ESR signals were sufficiently intense over the temperature range investigated so as to give signal-to-noise ratios of at least 25 : 1 when viewed on an oscilloscope screen. The peak positions of the transitions were measured to an accuracy of ±0.05 Oe. No other magnetic impurities were detected in the samples investigated.

III. RESULTS

The ESR absorption spectrum of divalent manganese substitutional for Ca^{2+} in $CaCO_3$ has been thoroughly investigated and documented.[30–35] The divalent manganese ion is located in a site of trigonal symmetry having as its nearest neighbors six carbonate ions. There are two inequivalent cation sites in the calcite structure associated with the alternation of the carbonate ion orientations in successive carbonate planes.[31–33] This inequivalence gives rise to a doublet splitting of each fine-structure transition when the Zeeman field is rotated away from the calcite [111] direction. All the data obtained in this investigation were taken with the Zeeman field along the calcite [111] axis where 30 resonance-absorption lines are observed. The spin Hamiltonian used to interpret the ESR data for this orientation is given by

$$\begin{aligned}\mathcal{H} &= g\beta H S_z + A I_z S_z + \tfrac{1}{2}B\left[I_+S_- + I_-S_+\right]\\ &\quad + D O_2^0 + a_0 O_4^0 + b_3 O_4^3 + (b_3 O_4^3)^* \ , \end{aligned} \tag{1}$$

where the spin operators O_n^m are given by

$$\begin{aligned} O_2^0 &= S_z^2 - \tfrac{1}{3}S(S+1) \ , \\ O_4^0 &= \tfrac{1}{180}\left[35S_z^4 - 30S(S+1)\,S_z^2 + 25S_z^2 \right.\\ &\qquad \left. - 6S(S+1) + 3S^2(S+1)^2\right] \ , \\ O_4^3 &= \tfrac{1}{4}\left[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z\right] \ . \end{aligned} \tag{2}$$

Rather than perform an exact diagonalization of the complex 36 × 36 matrix to obtain the energy eigenvalues, a perturbation calculation was performed by treating the operator $\frac{1}{2}B[I_+S_- + I_-S_+]$ as the perturbing term. Calculations were carried out up to fourth order and the hyperfine-coupling constant was taken to be isotropic, i.e., $A = B$.[30] Fourth-order terms were found to be small compared to second-order terms. In addition, second-order contributions from the operator $b_3O_4^3 + (b_3O_4^3)^*$ were found to be small compared to contributions from the hyperfine interaction, and were therefore neglected in the evaluation of the remaining parameters.[33] These approximations are justified in view of the fact that the calculated parameters fit all transitions to within the measured linewidths. The approximate energy eigenvalues to the Hamiltonian given by Eq. (1) are

$$\begin{aligned} E(\pm\tfrac{5}{2}, m) &= \pm\tfrac{5}{2}g\beta H \pm \tfrac{5}{2}Am + \tfrac{10}{3}D + \tfrac{1}{3}a_0 + E^2(\pm\tfrac{5}{2}, m), \\ E(\pm\tfrac{3}{2}, m) &= \pm\tfrac{3}{2}g\beta H \pm \tfrac{3}{2}Am - \tfrac{2}{3}D - a_0 + E^2(\pm\tfrac{3}{2}, m), \\ E(\pm\tfrac{1}{2}, m) &= \pm\tfrac{1}{2}g\beta H \pm \tfrac{1}{2}Am - \tfrac{8}{3}D + \tfrac{2}{3}a_0 + E^2(\pm\tfrac{1}{2}, m), \end{aligned} \tag{3}$$

where $E^2(M, m)$ are the second-order corrections to the eignestates evaluated from the expression

$$E^2(M, m) = \frac{A^2}{4}\left(\frac{(S-M)(S+M+1)(I+m)(I-m+1)}{E(M, m) - E(M+1, m-1)} + \frac{(S+M)(S-M+1)(I-m)(I+m+1)}{E(M, m) - E(M-1, m+1)}\right), \tag{4}$$

and (M, m) are the electron and nuclear magnetic quantum numbers, respectively. The energy differences in the denominators of Eq. (4) were evaluated to first order using negative signs for the parameters A, D, and a_0. The signs of D and a_0 were established from relative intensity measurements at low temperatures which show that the $\pm\frac{5}{2}$ spin states lie lowest in energy. This observation is consistent with results reported by Matarrese.[35,36]

Parameters calculated from the experimental data were obtained using only those transitions which were completely resolved. At least eight transitions were measured at each temperature, with a minimum of six data points on each line. The temperature dependences of D, a_0, and A are given in Figs. 1–3. Uncertainties in these results were estimated from the mean deviation of the calculated parameters about the average values obtained from the various transitions measured. There was no measurable temperature variation in the g value; however, the value that was measured, $g = 2.0015(3)$, agrees with that reported by Wait.[29] Also, no temperature variation was determined for b_3 since the evaluation of this parameter requires an analysis of the doublet splitting as a function of crystal orientation.[33]

The temperature variations of the spin-Hamiltonian parameters can be discussed in terms of implicit contributions resulting from lattice expansion and explicit contributions resulting from lattice vibrations.[15] If G is taken to be one of the measured parameters which is completely specified by the volume V and temperature T of the lattice, when held at constant pressure P, the temperature variation in G is given by

$$\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial G}{\partial T}\right)_V - \frac{\beta}{\kappa}\left(\frac{\partial G}{\partial P}\right)_T, \tag{5}$$

where the first term on the right-hand side is the explicit contribution to $G(T)$ and the second term on the right-hand side is the implicit term which may be evaluated if the isothermal pressure-dependent data are available. In addition, for calculational purposes it is necessary to assume that the local-volume-expansion coefficient β and the isothermal compressibility κ are those of the host lattice. The explicit contribution $G^*(T)$ can be related to the implicit contribution and the measured temperature variation $G(T)$ by integrating Eq. (5), giving

$$G^*(T) = G(T) + \int_0^T \frac{\beta}{\kappa}\left(\frac{\partial G}{\partial P}\right)_T dT. \tag{6}$$

The evaluation of the integral on the right-hand side of Eq. (6) was carried out using the hydrostatic pressure-dependent data reported by Wait[29] summarized below:

$$\begin{aligned} \frac{1}{D}\left(\frac{\partial D}{\partial P}\right)_{T=300\,^\circ\mathrm{K}} &= -7.1\times10^{-7}\ \mathrm{atm}^{-1}, \\ \frac{1}{a_0}\left(\frac{\partial a_0}{\partial P}\right)_{T=300\,^\circ\mathrm{K}} &= 7.3\times10^{-6}\ \mathrm{atm}^{-1}, \\ \frac{1}{A}\left(\frac{\partial A}{\partial P}\right)_{T=300\,^\circ\mathrm{K}} &= -1.7\times10^{-7}\ \mathrm{atm}^{-1}. \end{aligned} \tag{7}$$

The volume-expansion coefficient and isothermal

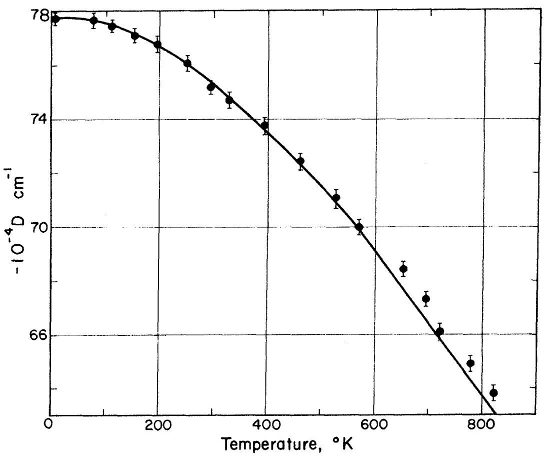

FIG. 1. Temperature dependence of the axial crystalline-field parameter D. The points are experimental, while the solid curve is the explicit temperature dependence after correcting for thermal expansion.

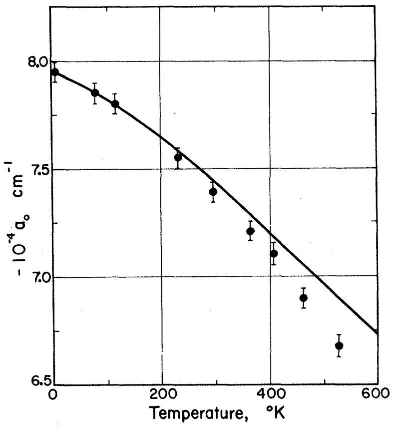

FIG. 2. Temperature dependence of the parameter a_0. The points are experimental, while the solid curve is the explicit temperature dependence after correcting for thermal expansion.

compressibility are both temperature dependent. Values for $\beta(T)$ were taken from two sources,[37,38] while values for $\kappa(T)$ were determined from the elastic constants of calcite.[39] Since the uncertainty in κ is about 15%, which is of the order of the change in κ over the temperature interval 0–250 °C, κ was assumed to be constant over the measured temperature range with an estimated uncertainty of 25%. Approximate values for β and κ are $20 \times 10^{-6} (°\mathrm{K})^{-1}$ and $15 \times 10^{-13} (\mathrm{dyn/cm^2})^{-1}$, respectively.

A. Temperature Dependence of D

The axial crystalline-field-splitting parameter D decreases by about 17% over the temperature range 4.2–800 °K (Fig. 1). Analyses of these data and the hydrostatic-pressure results, Eq. (7), show that the temperature dependence of D is predominantly due to explicit effects. Corrections to the data due to the implicit effects were carried out, and the resulting solid line in Fig. 1 represents the residual-temperature dependence associated with explicit effects. It is interesting to note that the temperature variations in D are very similar in magnitude and sign to the $D(T)$ data for substitutional $\mathrm{Fe^{3+}}$ in this host.[40] Unfortunately, hydrostatic-pressure data are not available for this impurity ion; hence it is not possible to make meaningful comparisons between the $\mathrm{Mn^{2+}}$ and $\mathrm{Fe^{3+}}$ results.

Although there are a large number of mechanisms which contribute to D,[1–13] the temperature variations may be interpreted in a semiquantitative fashion if one of the mechanisms is predominant. The relativistic mechanism proposed by Wybourne[12] and applied to the $\mathrm{Mn^{2+}}$ ion by Van Heuvelen[13] predicts the correct sign of D and its magnitude to within 15%. Though it is recognized that this agreement may well be fortuitous, it represents a means by which the present data may be understood. Briefly, the theory makes use of the point-charge model for the crystal-field calculations, where the axial term for a distorted octahedral environment is given by

$$V_{\mathrm{ax}} = A_2 r^2 C_2^0 , \tag{8}$$

where C_2^0 is a spherical harmonic proportional to Y_2^0 and the amplitude A_2 is given by[13]

$$A_2 = 7\mu/4\langle r^2\rangle = 7\delta/3\langle r^2\rangle . \tag{9}$$

The parameters μ and δ, obtained from optical experiments, are equal to the energy separations $E(b_{1g}) - E(a_{1g})$ and $E(b_{2g}) - E(e_g)$, respectively.[41] The operator $r^2 C_2^0$ is replaced by an operator involving single-particle double-tensor operators $W^{(ii')k}$ and radial integrals $b_k(ii')$.[12,13] The resulting contribution to the axial crystal-field-splitting energy is a second-order term given by

$$E^2(M) = \frac{\langle {}^6S_{5/2}M | \mathcal{H}_{\mathrm{so}} | {}^4P_{5/2}M \rangle \langle {}^4P_{5/2}M | A_2 b_2(11) W^{(11)2} | {}^6S_{5/2}M \rangle}{E({}^4P_{5/2}) - E({}^6S_{5/2})} , \tag{10}$$

where $\mathcal{H}_{\mathrm{so}}$ is the spin-orbit interaction. From this term, the following result is obtained for the relativistic contribution to D:

$$D_R = -\frac{3\lambda A_2}{125} \frac{0.0485}{E({}^4P_{5/2}) - E({}^6S_{5/2})} . \tag{11}$$

Substituting into Eq. (11) the parameters used by Van Heuvelen[13] gives $D_R = -0.009\ \mathrm{cm^{-1}}$.[42] This is to be compared with the experimental value $D = -0.0077\ \mathrm{cm^{-1}}$. Contributions to D from other mechanisms described in the literature are generally an order of magnitude smaller than this and have not been considered in this system.[1–11]

The temperature dependence of D is now treated using an approach suggested by Pfister *et al.*,[43] where p different normal vibrations are coupled to the amplitude A_2 of the axial crystalline-field parameter. In this treatment, the amplitude is expanded in a Taylor series using normal coordinates and the ground- and excited-state representations are written as the product of electronic and vibronic wave functions. The expansion of A_2 and the appropriate wave functions are then substituted into Eq. (10) and averages are taken over the ground-state vibrations using a harmonic approximation. The final result for the temperature dependence of D

is given by[43]

$$D(T)=D_0\left(1+\sum_{j=1}^{p}\frac{(\omega_j^2-\omega_j'^2)\hbar\coth(\hbar\omega_j/2kT)}{4\omega_j[E(^4P_{5/2},0)-E(^6S_{5/2},0)]}+\frac{1}{2A_2(0)}\sum_{j=1}^{p}\frac{\partial^2A_2}{\partial Q_j^2}\frac{\hbar}{2m\omega_j}\coth\frac{\hbar\omega_j}{2kT}\right). \tag{12}$$

The application of this result to the experimental data is, in general, a very complex problem, since it requires a knowledge of the normal-mode oscillations for the ground state as well as the vibrational frequencies ω_j' of the excited states. Also, it is usually not possible to measure second derivatives with respect to interionic spacings. To reduce these complexities it will be assumed that the ground- and excited-state vibrations are similar so that the first summation in Eq. (11) can be neglected. Second, it will be assumed that only one resonant vibration couples to the amplitude of the axial crystalline field, giving the following simplified expression:

$$D(T)=D_0+\delta\coth(\hbar\omega/2kT)\ . \tag{13}$$

This expression can be made to fit the experimental curve corrected for thermal expansion (Fig. 1) to within the experimental error with the parameters

$$D_0=-(86.3\pm0.8)\times10^{-4}\,\mathrm{cm}^{-1},$$

$$\delta=(8.5\pm0.8)\times10^{-4}\,\mathrm{cm}^{-1},$$

and

$$\omega=(8.5\pm0.5)\times10^{13}\,\mathrm{sec}^{-1}\ .$$

A similar analysis of the $D(T)$ data for Fe^{3+} in calcite, where the data extend from 4.2 to 300 °K,[40] yields the parameters

$$D_0=(333.4\pm1.0)\times10^{-4}\,\mathrm{cm}^{-1},$$

$$\delta=-(12.1\pm0.5)\times10^{-4}\,\mathrm{cm}^{-1},$$

and

$$\omega=(4.0\pm0.2)\times10^{13}\,\mathrm{sec}^{-1}\ .$$

Usually, optical studies of Mn^{2+} ions in ionic crystals show that a wide range of phonon frequencies can couple to the impurity ion. Therefore, the values for ω obtained here are perhaps more representative of an "averaged" phonon frequency. A more meaningful comparison between Mn^{2+} and Fe^{3+} might be realized if hydrostatic-pressure data were available for Fe^{3+} and if the predominant mechanism giving rise to D for this impurity was established.

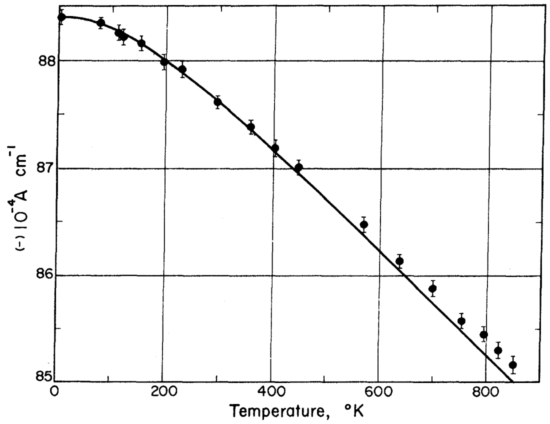

FIG. 3. Temperature dependence of the hyperfine-coupling parameter A. The points are experimental, while the solid curve is the explicit temperature dependence after correcting for thermal expansion.

B. Temperature Dependence of a_0

Results of the temperature variations of the parameter a_0 are given in Fig. 2. The contribution to $a_0(T)$ from implicit effects was calculated to be

$$\frac{\beta}{\kappa}\frac{1}{a_0}\left(\frac{\partial a_0}{\partial P}\right)_T\cong10^{-4}\,(^\circ\mathrm{K})^{-1},$$

whereas the measured temperature variation was found to be

$$\frac{1}{a_0}\left(\frac{\partial a_0}{\partial T}\right)_P\cong-4\times10^{-4}\,(^\circ\mathrm{K})^{-1}\ .$$

Therefore, the explicit contribution given by the solid line in Fig. 2 is calculated to be

$$\frac{1}{a_0}\left(\frac{\partial a_0}{\partial T}\right)_V\cong-3\times10^{-4}\,(^\circ\mathrm{K})^{-1}\ .$$

This result suggests that explicit effects are predominant in the temperature variation of a_0. Even if the local values of β and κ are assumed to be substantially different from those of calcite, explicit contributions would still be significant.

The parameter a_0 is related to the cubic-field-splitting parameter a through the relation $a-F=-a_0$; therefore, temperature variations in a_0 are due to variations in both a and F. Generally, F is observed to be smaller in magnitude than a; therefore, on this basis it can be concluded that a is positive. If a varies as the nth power of the cubic field Dq, then $a\sim V^{-5n/3}$, where V is the volume of the polyhedra formed by the nearest neighbors. This result follows from the point-charge model in which $Dq\sim r^{-5}$ or $Dq\sim V^{-5/3}$. The implicit contribution to $a(T)$ can then be written as

$$\frac{1}{a}\left(\frac{\partial a}{\partial P}\right)_T=-\frac{5n}{3}\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T=-\frac{5n}{3}\kappa\ . \tag{14}$$

It is difficult to determine the power dependence of a on Dq from these considerations, since the local value of κ may be significantly different from the bulk value. If $n=2$ as suggested by Watanabe,[3] and the local value of κ is taken to be equal to the bulk value, the right-hand side of Eq. (14) is given by $-5\times10^{-12}\,(\mathrm{dyn/cm}^2)^{-1}$, while the corresponding experimental value is -7.5×10^{-12} $(\mathrm{dyn/cm^2})^{-1}$. However, if the local value of κ is taken to be 50% greater than the bulk value, the above analysis would suggest that $a\sim(Dq)^2$. On the other hand, if the local value of κ is taken to be 50% less than the bulk value, the analysis would suggest that $a\sim(Dq)^4$. The second choice appears to be physically more meaningful since the ionic radius of Mn^{2+} is less than that of Ca^{2+}; hence the crystal should be "softer" in the vicinity of the impurity. This is qualitatively consistent with results obtained for Mn^{2+}, Eu^{2+}, and Gd^{3+} in cubic crystals,[15,44,45] Eu^{2+} in noncubic sites of $CaWO_4$,[46] and Fe^{3+} in $CaCO_3$.[40,47] Hence, the mechanism proposed by Watanabe does not appear to be an important contribution to the cubic-field splitting of Mn^{2+} in $CaCO_3$.

According to the theory of Gabriel *et al.*,[7] the cubic-field-splitting parameter should vary as $\lambda^4(Dq)^n$, where n ranges from 3 to 6 depending on the value of Dq. Using the value $Dq=880$ cm^{-1} reported[48] on the optical spectrum of $MnCO_3$ and taking $\lambda=300$ cm^{-1} gives $a\cong5.2\times10^{-4}$ cm^{-1}.[49] The value of n is close to 4 for this choice of Dq. Obviously, the calculated value of a is very sensitive to the choice of λ; e.g., if λ is taken to be 270 cm^{-1}, $a\cong3.6\times10^{-4}$ cm^{-1}. At any rate, our measured value of a_0 (assumed to be approximately equal to $-a$) is somewhat larger than the calculated value of a, but of the correct sign. Other investigators have found the opposite to be the case for Mn^{2+} in axially symmetric environments.[49] The present results appear to be in qualitative agreement with the predictions of this theory.

C. Hyperfine-Coupling Temperature Dependence

The hyperfine-coupling constant A is observed to decrease by about 3% over the temperature interval 4.2–800 °K (Fig. 3). This general behavior has been observed and analyzed for Mn^{2+} in a variety of cubic environments.[15–27] The contribution to the hyperfine-coupling temperature dependence from implicit effects is seen to be small and of the opposite sign to the observed $A(T)$ data (Fig. 3). Therefore, it is concluded that the temperature variation in A is due primarily to explicit effects.

The only quantitative approach which has been taken to explain hyperfine-coupling temperature variations for S-state ions is the mechanism proposed by Simanek and Orbach.[16] Unfortunately, the theory applies only to cubic environments; hence there is no justification in applying the results to the Mn^{2+}:$CaCO_3$ system. However, it is interesting to determine whether or not the theoretical expression for $A(T)$ is at least functionally correct. When the lattice vibrations are described by a Debye model, the hyperfine-coupling temperature dependence for an S-state ion is given by[16]

$$A(T)=A(0)\left(1-CT^4\int_0^{\Theta/T}\frac{x^3\,dx}{e^x-1}\right), \tag{15}$$

where $A(0)$ is the hyperfine-coupling constant at 0 °K, Θ is the averaged Debye temperature, and C is a complex coefficient which can be estimated from the effective point-charge model. The experimental data, corrected for thermal expansion, were fitted with this expression, treating both C and Θ as adjustable parameters. Such an analysis yields the values $C=1.16\times10^{-12}$ $(^\circ\mathrm{K})^{-4}$ and $\Theta=530$ °K and produces a good functional fit to the data to within experimental error. The fit is quite sensitive to Θ over the entire temperature range, and a choice of Θ outside the interval 510–550 °K results in a curve which does not coincide with the experimental curve within the uncertainties indicated. There is some difficulty in determining the averaged Debye temperature for calcite. Low-temperature specific-heat measurements yield a value $\Theta=210$ °K,[50] while elastic constants measured at room temperature produce a value $\Theta=469$ °K.[51] Presumably, at low temperatures molecular vibrations do not contribute significantly to the specific heat, whereas the room-temperature measurements of the velocity of sound are sensitive to such excitations. However, even in an extreme case, the choice of $\Theta=469$ °K does not provide a fit to the experimental data to within the experimental error.

An alternative explanation of the $A(T)$ data is the assumption of the large-amplitude-resonance mode which couples the Mn^{2+} electronic states to the lattice. Such a mode can produce a mixing of excited ns states into the ground $3d$ state, giving rise to a net decrease of the hyperfine field.[24,52] If this resonance mode has even symmetry, such that the impurity ion is stationary while the lattice vibrates with a large amplitude, the effective-force constant can be greatly reduced in the region of the impurity ion. Such a modification of the continuous phonon spectrum has been suggested in the interpretation of the $A(T)$ data for Mn^{2+} in SrO[24] and BaO,[52] where the Mn^{2+} ionic radius is much smaller than that of the cation. The temperature dependence of A using this description can be written as[52]

$$A(T)=A(0)\left(1-\frac{C'}{e^{\hbar\omega/kT}-1}\right), \tag{16}$$

where this result is based upon the average value of the square of the displacement for the harmonic oscillator. This function can be fitted to the experimental data with the parameters $\omega=(5.1\pm0.3)\times10^{13}$ sec^{-1} and $C'=(2.23\pm0.20)\times10^{-2}$, where $A(0)=(-)88.40\times10^{-4}$ cm^{-1}. With these parameters and the functional form of $A(T)$ given by Eq. (16), the theoretical curve agrees with the solid curve in Fig. 3 to within $\pm0.05\times10^{-4}$ cm^{-1} over the entire temperature interval. It is interesting to note that Eqs. (13) and (16) have the same functional forms and are derived in similar fashions. Perhaps the different frequencies obtained in the two cases may be due to the fact that only resonance modes of even parity can contribute to $A(T)$.

IV. DISCUSSION

The results presented in Sec. III demonstrate the importance of explicit effects in the temperature variation of the spin-Hamiltonian parameters for Mn^{2+} in trigonal sites of $CaCO_3$. Implicit contributions to the $D(T)$ and $A(T)$ data have been shown to be small and opposite in sign to the experimentally observed temperature variation. Since a rigorous description of the exact nature of the explicit temperature variations is an extremely complex problem, attempts have been made to present a semiquantitative interpretation of the results. An analysis of the axial crystalline-field temperature dependence, which regards the relativistic mechanism as the predominant effect giving rise to D, suggests that resonant vibrations couple to the impurity ion through the amplitudes of the crystalline-field potential.[43] Obviously the assumptions that have been made in arriving at an averaged phonon frequency lead to a great oversimplification of the problem. A more sensitive test of the theory might be realized if the normal vibrations which couple to the impurity ion were known. Temperature variations in D for charge-compensated Cr^{3+} ions in MgO were tentatively attributed to thermal-expansion effects, contrary to our conclusions.[15] The difference in the two interpretations may arise from the fact that for Cr^{3+}: MgO, where a local charge compensator is present along one of the cube axes, small changes in the local ionic separations could give rise to large changes in D. However, in the present system no charge compensation is necessary and presumably the axial crystalline field is rather insensitive to thermal expansion. In other words, the comparison suggests that the predominant mechanisms giving rise to D in the two systems are quite dissimilar.

Temperature variations in the parameter a_0, which were taken to be a measure of the temperature dependence of the cubic-field-splitting parameter, also suggest a large explicit effect. The relativistic mechanism predicts a cubic-field splitting which is about an order of magnitude smaller than the experimentally observed value.[13] An analysis of the pressure variations of the parameter a_0 indicates that the cubic-field-splitting parameter is proportional to $(Dq)^n$, where $2 \leq n \leq 4$ depending on the value chosen for the local isothermal compressibility. Both the magnitude of a and the power dependence on Dq are in qualitative agreement with calculations by Gabriel, Johnston, and Powell.[7]

The decrease in the hyperfine-coupling constant with increasing temperature is similar to that found for Mn^{2+} in a number of sixfold and eightfold coordinated cubic environments. Since the local symmetry of Mn^{2+} in $CaCO_3$ is trigonal, there is no justification in making use of the Simanek-Orbach expression for $A(T)$ which applies to cubic environments. Such an expression has been shown to fit the data only if a Debye temperature is chosen which is substantially greater than experimentally measured values. An alternative approach in the interpretation of the $A(T)$ data is to assume that a large-amplitude local mode couples to the hyperfine interaction and that such an interaction overwhelms the continuous Debye phonon spectrum. It is interesting to point out that the local-mode frequency obtained from this analysis, $\omega = 5.1 \times 10^{13}$ sec^{-1}, is about 30% smaller than the averaged phonon frequency obtained from the analysis of the $D(T)$ data. The comparison suggests that a complete normal-mode treatment is necessary in interpreting the $D(T)$ data. Perhaps additional information on the importance of large-amplitude local modes might be obtained from a more detailed investigation of $D(T)$ and $A(T)$ at low temperatures.

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