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Temperature Dependence of the Hyperfine Coupling of Mn^{2+} in the Oxides: Experimental and Theoretical*

R. Calvo†
University of California, San Diego, La Jolla, California
AND
R. Orbach‡
University of California, Los Angeles, California

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We have measured the temperature dependence of the hyperfine constant of $(Mn^{55})^{2+}$ in CaO and SrO between 1.4 and 300°K. Our experimental data are in good agreement with the Debye model due to Simanek and Orbach; we give the parameters obtained from the best fit of experiments with theory. Also, by using a semiempirical model to evaluate the amplitude of the lattice vibrations, we have been able to evaluate directly the constants of the orbit-lattice interaction. With both the Debye model and the semiempirical model, we have evaluated the decrease of the hyperfine constant by the zero-point vibrations. We find that the zero-point phonon contribution is larger in CaO than in SrO.

I. INTRODUCTION

THE temperature dependence of the hyperfine coupling of Mn^{2+} in various crystalline lattices (MgO, ZnO, ZnS, CdTe, and $KMgF_3$) has been measured by Walsh, Jeener, and Bloembergen.[1] These authors found that the hyperfine constant varied with temperature in the opposite direction from that expected from thermal expansion. To explain this behavior Simanek and Orbach[2] proposed a mechanism in which s-like configurations are admixed into the $3d^5$ configuration by the orbit-lattice interaction. Using a Debye model for the thermal vibrations of the crystal, these authors obtained for MgO a temperature dependence of the hyperfine constant in good agreement with the experimental values of Walsh *et al.*[1]

Continuing this study of the hyperfine-constant temperature dependence, Rosenthal, Yarmus, and Bartram investigated its behavior in NaCl,[3] CaO, and SrO.[4] Their experimental results for NaCl and CaO are in agreement with the theory.[2] However, for SrO they found a linear dependence of A with temperature; this is in disagreement with the theory which predicts that A must be nearly constant at low temperatures.

The data of Rosenthal *et al.*[4] were taken between 300 and 1000°K. Below 300°K, they completed their temperature-dependence curve with a few points obtained from the work of other experimentalists. This low-temperature region is precisely where their curve for SrO shows lack of agreement with the theory. We therefore undertook to extend the measurements to the range of temperature between 1.4 and 300°K, taking all the data with the same sample and the same experimental setup. Thus, with good curves in this temperature region, which is the most sensitive to the model used, we can check the limits of validity of the Debye model.

Using the Deby model of the lattice, there are three adjustable parameters with which to fit the experimental data. In order to improve on this model and in an effort to obtain a more physical picture of the mechanisms involved, we propose (following Orbach and Simanek[5]) a linear diatomic chain model of the lattice. This "semiempirical" model allows us to obtain the constants that give a direct measure of the orbit-lattice interaction of Mn^{2+} in the isomorphous lattices MgO CaO, and SrO.

II. EXPERIMENT

The crystals we used were obtained from Semi-Elements, Inc. They were quoted as undoped and thus the manganese was an unintended impurity in the lattice.

The measurements were performed in a superheterodyne spectrometer working at 9200 MHz.[6] In order to cover the range of temperature between 77 and 300°K, we used a copper cavity heated by a noninductive resistance.

We obtained the values of the hyperfine constant A from the spin Hamiltonian given by Low[7] considering the contributions up to third order in a perturbation calculation.[8]

In Figs. 1 and 2, we have plotted the experimental values of the hyperfine constant of Mn^{2+} in CaO and SrO, respectively.

The accuracy of our measurements of the hyperfine constant A is 0.02% or better. The uncertainty in the

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‡ Alfred P. Sloan Foundation Fellow.

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temperature is big only between 77 and 300°K where we estimate it to be 2°K.

In the course of these experiments we studied the linewidth temperature dependence of the fine-structure transition $M_s = -\frac{1}{2} \leftrightarrow \frac{1}{2}$. We found for Mn^{2+} in CaO a linewidth of 30 mG at 1.4°K and 500 mG at 300°K. Between 77 and 300°K, we observed a Raman-like temperature dependence of the linewidth. We attribute the linewidth in this temperature range to a spin-lattice relaxation. This behavior contrasts with that of Mn^{2+} in MgO where the linewidth is nearly independent of temperature. For Mn^{2+} in SrO, the observed linewidth was of the order of 1 G at helium temperatures and only slightly broader at room temperatures. We believe it is due to the unresolved fine structure.

In the temperature range between 1.4 and 300°K, the value of the gyromagnetic factor was constant and the same for both lattices, CaO and SrO, within the experimental error. We obtain

$$g = 2.00145 \pm 0.00015.$$

III. THEORY

The mechanism proposed by Simanek and Orbach[2] to explain the experimental data,[1] is one that admixes *s*-like configurations into the $3d^5$ configuration by the thermal vibrations through the orbit-lattice interaction. This mechanism gives a change of the hyperfine constant that is proportional to the mean value of the square of the amplitudes of vibrations $\langle Q^2 \rangle$ (an average over the different normal modes). Then the hyperfine constant at temperature T is given by

$$A(T) = A_{\mathrm{RL}} + c\langle Q^2 \rangle(T), \qquad (1)$$

where A_{RL} is the hyperfine constant for a rigid lattice, and c is the constant of the interaction.

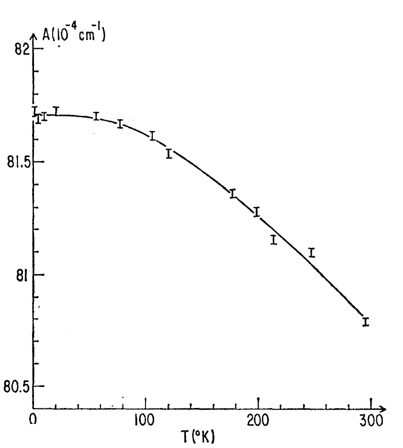

FIG. 1. Temperature dependence of the hyperfine constant of $(Mn^{55})^{2+}$ in CaO. The solid line gives the best fit with a Debye model for the crystal.

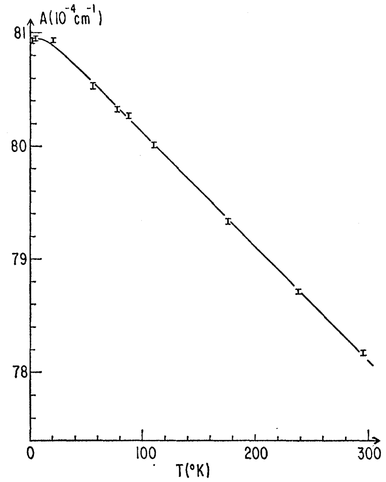

FIG. 2. Temperature dependence of the hyperfine constant of $(Mn^{55})^{2+}$ in SrO. The solid line gives the best fit with a Deybe model for the crystal.

A. The Debye Model

Using a Debye model for the lattice vibrations, the following expression is obtained[2]:

$$A(T) = A(0)\left[1 - CT^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}\right]. \qquad (2)$$

In this expression, Θ is the Debye temperature of the crystal;

$$A(0) = A_{\mathrm{RL}} + c\langle Q^2 \rangle(0)$$

is the hyperfine constant at 0°K; and C is a constant that depends on the orbit-lattice interaction and also on the vibrational properties of the crystal. Using (2), we can find for each crystal the values of $A(0)$, Θ, and C which fit the experimental data.

It is possible with the Debye model to find values for the zero-point phonon decrease of the hyperfine constant ΔA. We find

$$\Delta A = c\langle Q^2 \rangle(0) = -\tfrac{1}{8} A(0) C \Theta^4. \qquad (3)$$

Then $A_{\mathrm{RL}} = A(0) - \Delta A$ gives the hyperfine constant for a rigid lattice as a function of $A(0)$, Θ, and C.

B. The Semiempirical Model

Rather than the constant C obtained with the Debye model, it would be physically more meaningful to obtain the constant c defined by (1). The latter is related directly to the orbit-lattice interaction and is independent of the vibrational properties of the lattice.

However, in order to evaluate it, we need a more specific model of the lattice than the Debye model. Following Orbach and Simanek[5] in their calculations of the zero-point phonon decrease of the hyperfine constant, we use a linear diatomic chain model of the lattice extended to three dimensions.

This semiempirical model of the crystal allows us to compute the amplitude of the normal vibrations which can interact with the impurity and change the hyperfine constant. With these values and the experimental data of Figs. 1 and 2, we are then able to evaluate the interaction constant c.

In this model, the phonon dispersion relations are given by

$$\omega^2(k)=\mu/mM\{m+M\pm[M^2+m^2+2mM\cos(ka)]^{1/2}\},$$

where m and M are the mass of the anion and cation, respectively, k is the moment of the phonon, a is the lattice parameter, and μ is the force constant. The $\pm$ sign refers to acoustical and optical phonons.

We find the values of $\langle Q^2\rangle$, the mean value of the square of the amplitude of the lattice normal vibration responsible for the interaction, and also of $\langle q^2\rangle$; q is the displacement of the ion from its equilibrium position and Q is defined by $Q=\frac{1}{2}(q_{2n+1}-q_{2n-1})$, where $2n+1$ and $2n-1$ give the position of the ions on the linear chain.

The mean values of q^2 and Q^2, in units of the lattice parameter, are found to be

$$\langle q^2\rangle=\frac{1}{a^5}\frac{\hbar}{\pi^2}\frac{V}{Nm}\sum_p\int_0^\pi[\omega(y)]^{-1}\alpha^2(y)(n[\omega(y)]+\tfrac{1}{2})y^2dy \tag{4}$$

and

$$\langle Q^2\rangle=\frac{1}{a^5}\frac{\hbar}{\pi^2}\frac{V}{Nm}\sum_p\int_0^\pi[\omega(y)]^{-1}\alpha^2(y)\times(n[\omega(y)]+\tfrac{1}{2})y^2\sin^2 y\,dy, \tag{5}$$

where

$$y=ka,\qquad n[\omega(y)]=\left[\exp\left(\frac{\hbar\omega(y)}{kT}\right)-1\right]^{-1}$$

is the Bose factor,

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

and $\sum_p$ means summation over the different branches of phonons. In (4) and (5), we have made a spherical approximation like that used by Orbach and Simanek.[5]

The elastic constants of the crystal and the optical frequencies of phonons with zero moment are given in this model by

$$C_0=\rho\mu/2(m+M), \tag{6}$$

$$\omega^2(k=0)=2(m^{-1}+M^{-1})\mu, \tag{7}$$

where C_0 is the elastic constant, ρ is the density of the crystal, and $\omega(k=0)$ is the frequency of phonons with zero moment.

However, in order to fit this simple model to the experimental data, we find that one force constant is not sufficient. We therefore introduce different force constants for the longitudinal and transverse branches of phonons and different force constants for the acoustical and optical branches. The first consideration allows us to take into account the different phonon polarization branches. The second consideration has been introduced because when we compare (6) and (7) with the experimental data for MgO,[9–11] we see that it is impossible to explain both the acoustical and optical branches, with the same force constant.

It is necessary then to evaluate the four force constants for each crystal from the elastic constant and optical data. Unfortunately, we have all the information we need[9–12] only for MgO. For the other two hosts there are no data on the elastic constants and the lattice vibrational frequencies are not known. Thus we must rely on data for the optical frequencies[13] which are not trustworthy, since they were published simultaneously with information for MgO which has been shown to be incorrect.[9]

For MgO, where we have experimental data of elastic constants and optical frequencies, we obtain good agreement between our calculated values and those obtained from x-ray measurements. For CaO, the absence of reliable phonon dispersion frequencies resulted in force constants for our model which yield vibrational amplitudes some 20% less than those observed with x rays. For SrO there are no x-ray data to compare with our calculations.

We try to remedy this abscence of information for CaO by correcting the calculated values of $\langle Q^2\rangle$ comparing the measured values by x-ray techniques,[12] and our calculated $\langle q^2\rangle$. With the corrected values of $\langle Q^2\rangle$

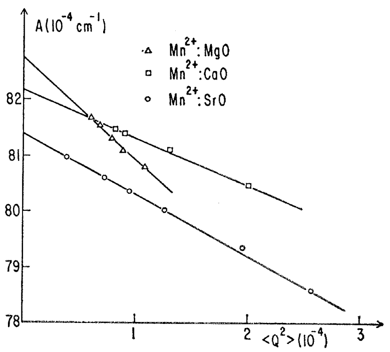

FIG. 3. Experimental values of the hyperfine constant A as a function of our calculated $\langle Q^2\rangle$. Each point corresponds to one temperature. Q is in units of the lattice parameter a. The experimental points for Mn^{2+} in MgO from Ref. 1 are the symbols □.

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TABLE I. Hyperfine-coupling data fitted with a Debye model. Values for the Debye temperature Θ_D, the zero-phonon contribution to the hyperfine constant ΔA, and the rigid lattice value of the hyperfine constant A_{RL}.

Crystal	Θ_D (°K)	C(°K^{-4})	$A(0)$ (10^{-4} cm^{-1})	ΔA (10^{-4} cm^{-1})	A_{RL} (10^{-4} cm^{-1})
MgO[a]	750	2.58×10^{-13}	-81.55	0.83	-82.38
CaO[b]	450	2.30×10^{-12}	-81.707	0.964	-82.67
SrO[b]	70[c]	1.274×10^{-9}	-80.948	0.31	-81.26
	50[d]	2.996×10^{-9}	-80.946		

[a] From Ref. 1. [b] Our data. [c] Low-temperature fitting. [d] Entire range fitting.

and our experimental data, we find the constants A_{RL} and c from the relation (1). We list the constants obtained in Table II.

IV. RESULTS AND DISCUSSION

Figures 1 and 2 display our data for the temperature dependence of the hyperfine constant of Mn^{2+} in CaO and SrO. Since there are no hydrostatic-pressure experimental data for Mn^{2+} in these lattices, we cannot correct for the thermal expansion of the crystal. Our estimate, based on data for MgO, shows that this correction is of the order of our experimental error in the temperature range we have covered.

The solid lines in Figs. 1 and 2 give the fitting (smallest mean-square deviation) with the Debye relation (1), and Table I summarizes the values of the parameters used. For CaO between 1.4 and 300°K, we obtain a Debye temperature, $\Theta=450$°K, in reasonable agreement with tabulated data. For SrO, we obtain $\Theta=50$°K if we consider the whole range of temperature. (For the low-temperature range, between 1.4 and 77°K, better agreement is obtained with $\Theta=70$°K.) Thus, we find that the Debye dependence is obeyed and $A(T)$ is essentially constant below 20°K for SrO. This behavior could not be detected in the curve of Rosenthal *et al.*[4]

Although there are not available data in the literature with which to compare them, our values of the Debye temperature for SrO seem to be anomalously low. An explanation for this may lie in the difference in size between the Mn^{2+} and the Sr^{2+} ions: Since the Mn^{2+} are much smaller than the Sr^{2+} ions which they replace, this would tend to make the crystal softer in the region of the impurity. It may also be important to consider the changes of the O^{2-} wave functions in different potential environments as was pointed out by Orbach and Simanek.[5]

We also list in Table I the contribution ΔA of the zero-point vibration to the hyperfine constant change. The values given were obtained from (3), using the parameters given in Table I.

TABLE II. Coupling constant c, zero-phonon contribution ΔA, and rigid-lattice value A_{RL} of the hyperfine constant. Values obtained from our semiempirical model.

Crystal	ΔA (10^{-4} cm^{-1})	A_{RL} (10^{-4} cm^{-1})	c (cm^{-1})
MgO	0.6	-82.15	0.88
CaO	1.04	-82.75	1.8
SrO	0.5	-81.45	1

Figure 3 gives the experimental values of the hyperfine constant A as a function of $\langle Q^2\rangle$ obtained from our semiempirical model, where each point corresponds to one temperature. It can be seen that the dependence is approximately linear [as expected from Eq. (1)] for the three crystals. We found from this figure the values for the interaction constant c, the zero-point phonon contribution to the hyperfine constant ΔA, and the hyperfine constant corresponding to a rigid lattice, which are given in Table II.

For the interaction constant c, we find a higher value for CaO than for MgO and SrO. It would be interesting to compare these values with values of c obtained experimentally. This could in principle be done by a uniaxial stress experiment. Assuming an applied deformation[14] of the order of 10^{-4} we find, using the values of Table II, that the changes of the hyperfine constant would be $\Delta A/A\approx10^{-6}$. We believe that this order of magnitude would be difficult if not impossible to measure even in an ENDOR uniaxial stress experiment.

For ΔA and A_{RL}, we find (Tables I and II) that both models give consistently higher values for CaO than for SrO and MgO (even if both models give different absolute values).

We find a large difference between our value of ΔA for SrO (Table II) and the results of Orbach and Simanek.[5] We believe that this discrepancy is due to our respective choice of force constants and that the model is very sensitive to this choice. The force constants are determined from the phonon-dispersion curves, or elastic constant and optical frequencies, which are data that are not available for SrO. More experimental information is needed, therefore, before this discrepancy can be removed.

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[14] This is the largest deformation that can be introduced in MgO without breaking the sample. For these deformations, E. R. Feher [Phys. Rev. **136A**, 145 (1964)] did not observe any change in the hyperfine constant within the experimental error

$$(\Delta A/A=0.01\%).$$