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Energy of the First Excited Electronic Level(s) of Fe^{2+} in CaO†‡

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The electron-spin recovery time τ has been observed for low concentrations of Fe^{2+} ions in CaO in fields of about 1800 G from 1.3 to 4.1 K; line broadening at 8.9 GHz has been measured from 7 to 15 K. The temperature dependence of τ and the linewidth give the energy of the first excited state(s) to be 23.9 ± 1.5 cm^{-1}, indicating strong orbital reduction, probably due to dynamic Jahn-Teller distortions. The observed bottleneck generated at 9, 18, and 700 GHz by pulse saturation at 9 GHz is consistent with earlier observation of intrinsic spin-lattice relaxation of Fe^{2+} at similar concentrations in MgO.

INTRODUCTION

The configuration of Fe^{2+} is $3d^6$ and in an octahedral field the ground state is an orbital triplet (Γ_{5g}). The point-charge crystal field model estimates the lowest excited states Γ_{3g}, Γ_{4g} to be at $2|\lambda|$, where λ, the free-ion spin-orbit coupling parameter, is ~ 100 cm^{-1}. With the same model the g value of the ground state is predicted to be ~ 3.5. Any orbital reduction[1] will reduce both the energy of the first excited states and the g value of the ground state.

The measured g value of the Fe^{2+} ion in CaO is 3.298,[2] and in MgO it is 3.428.[3] Early interpretation of the g shift attributed the orbital reduction to covalency in MgO[4] and CaO.[2] However, Ham has pointed out[5] that covalent effects on the orbital reduction should be smaller in CaO due to the larger lattice spacing a_0. Measurement[6] of the isomer shifts in Fe^{2+} in CaO and MgO by Chappert *et al.* indicate the effects of covalency to be less in CaO.

Ham suggested[7] the dynamic Jahn-Teller effect[8] to be the mechanism for this reduction. The dynamic Jahn-Teller effect should be stronger in CaO than in MgO,[8] since the effect varies inversely with phonon frequency, and the larger a_0 in CaO will depress the values of the effective phonon frequency.

The energy of the first excited state of Fe^{2+} in MgO has been observed independently by infrared spectroscopy[9] and spin-lattice relaxation[10] and was found to be ~ 100 cm^{-1}. Assuming Ham's suggestion of the dynamic Jahn-Teller effect is correct, we would expect to find in CaO the energy of the first excited state to be lower and the spin relaxation via an Orbach process to be even stronger. The purpose of this paper is to present the data from which we find the energy of the first excited state(s) of Fe^{2+} in CaO. The results are given after a brief discussion of the two microwave relaxation techniques employed.

EXPERIMENTAL

Pulse saturation recovery[11] and line broadening[12] have been observed on the $\Delta m = 1$ transition of Fe^{2+} in CaO at a frequency of 8.9 GHz in two samples.

The absolute value of the concentration of Fe^{2+} was estimated for sample 1 by comparison of its electron-paramagnetic-resonance (EPR) signal, obtained from a previously calibrated MgO sample.[12,13] The relative concentration of sample 1 to sample 2 was measured using Thermax[14] powder sealed in a thin plastic envelope as a secondary standard.

The spin-recovery data were taken at 1880 G by the pulse-saturation method using 100 mW of pulse power and 1 μW of monitoring power. The traveling-wave tube spectrometer[15,16] used in this experiment can measure recovery time τ as short as 0.2 μsec. For τ greater than 5 μsec, recovery signals were extracted using a Waveform Eductor[17] and a logarithmic converter. This ap-

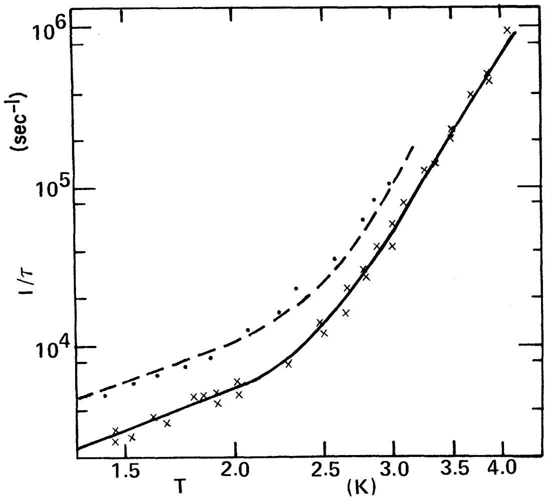

FIG. 1. Reciprocal of the asymptotic spin recovery time τ of CaO at 1880 G vs temperature. Both scales are logarithmic. The data from sample 1 are represented by × and the data from sample 2 are represented by ● . The solid curve is a least-squares fit of Eq. (1) to the data of sample 1. The dashed curve was obtained by multiplying Eq. (1) by 2.0 (the ratio of the concentration of Fe^{2+} in sample 1 to that of sample 2). The experimental uncertainty for the τ values was approximately ±10% and the experimental error in the temperature was negligible.

paratus has been previously discussed in the literature.[10,12] For τ less than 5 μsec the recovery was photographed directly from an oscilloscope and plotted on semilog paper. On the basis of reproducibility, the experimental uncertainty in the recovery time was judged to be less than ±10%.

The line-broadening data were taken with the static magnetic field parallel to [111]. In this orientation, each sample had its minimum residual linewidth ΔH_0 of 170 G.

The temperature of the He bath was measured by its vapor pressure. The temperature of the cavity wall next to the sample was monitored by a 270-Ω 0.1-W Allen Bradley carbon resistor[18] calibrated at 2.0, 4.2, and 21.2 K and fitted to a semiempirical equation[19] which yields a calibration within ± 0.5% of the absolute value of the temperature.

RESULTS

The concentration of Fe^{2+} in sample 1, c_1, was found from the EPR signal to be 200 ppm. Using Thermax[14] as an EPR standard, the relative concentration of sample 1 to sample 2 was found to be 2.0 ± 0.6.

At each temperature from 1.3 to 2.5 K, the recovery at 1880 G from pulse saturation was a rapid decay followed by a longer asymptotic exponential decay. The zero-time intercept for the latter portion of a recovery at $T \sim 2$ K was 50% of saturation for sample 1. The time constant of the asymptotic section of the recovery is labeled by τ. The temperature dependence of $1/\tau$ in this region shown in Fig. 1 is well described by AT^2, where A is a constant which was found to be inversely proportional to the Fe^{2+} concentration c. The accuracy of this proportionality is limited by the uncertainty in the values of c. For each of several temperatures, the recovery was observed to have the identical shape at several positions of the static magnetic field within the $\Delta m = 1$ transition, including the position of the double quantum transition.[20] The value of τ was found to be independent of crystal orientation in the magnetic field, in contrast to the angular dependence found for the intrinsic process of Fe^{2+} in MgO by Lewis.[21]

Above 2.6 K each recovery was observed to be a single exponential decay. The temperature dependence is described by $B(e^{\Delta/T} - 1)^{-1}$, where $\Delta = 34$ K and the constant B is inversely proportional to c and independent of orientation.

The solid curve in Fig. 1 shows a plot of the theoretical expression

$$1/\tau = AT^2 + B(e^{\Delta/T} - 1)^{-1} , \qquad (1)$$

for a least-squares fit of Eq. (1) to the recovery data of sample 1. The values of the constants obtained along with their standard error values were $A = (1.33 \pm 0.03) \times 10^3$ sec^{-1} K^{-2}, $B = (34.2 \pm 0.07) \times 10^9$ sec^{-1}, and $\Delta = 34.3 \pm 0.7$ K, with a standard deviation[22] $\sigma = 0.088$. For comparison, the experimental uncertainty in each value of τ is ±10%, as discussed earlier.

It should be pointed out that the observed values of $1/\tau$ follow very closely T^7 for T above 2.6 K, as shown in Fig. 1. The normal Raman processes

$$\frac{1}{\tau} = A_5\left(\frac{T}{\Theta_D}\right)^5 J_4\left(\frac{\Theta_D}{T}\right) + A_7\left(\frac{T}{\Theta_D}\right)^7 J_6\left(\frac{\Theta_D}{T}\right) \qquad (2)$$

have not been used in Fig. 1 since the theoretical values of the terms in Eq. (2) are several orders of magnitude too small to contribute to the observed recovery rate. The Θ_D value to be used[23] is known from optical data[24] on CaO.

The recovery data for sample 2 is well fitted by multiplying the right-hand side of Eq. (1) by 2.0, the ratio of the Fe^{2+} concentrations. The fit is shown by the dashed line in Fig. 1. The standard deviation of this curve from the data of sample 2 is 0.11, also comparable to our experimental scatter. The fact that both coefficients vary inversely with c demonstrates the presence of a phonon bottleneck in both the direct and Orbach processes at these concentrations.

Sample 1 was cleaved reducing its smallest

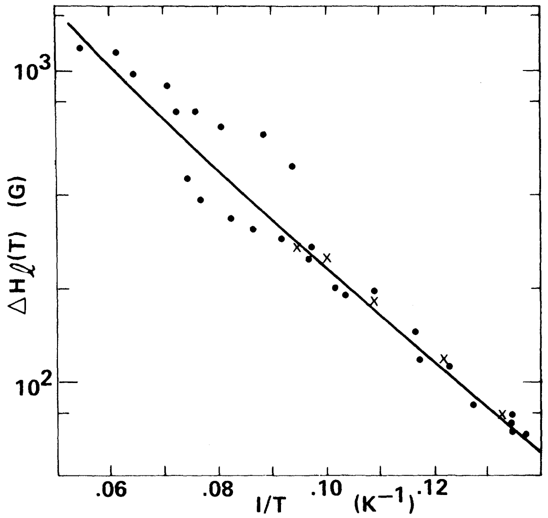

FIG. 2. Lifetime broadening linewidth $\Delta H_l(T)$ calculated by Eq. (3) vs the reciprocal of the temperature T. The data from sample 1 are represented by × and the data from sample 2 are represented by ●. The solid curve is $(7.1\times10^3\ \text{G})\ (e^{34.2/T}-1)^{-1}$. The scatter in the data above 10 K is due to the presence of the $\Delta m=2$ transition near 900 G.

dimension by half to 1.0 mm. Spin recovery measurements were taken at 1.8 and 3.0 K; the values obtained were unchanged within experimental uncertainty.

At 4.2 K, the EPR line shape is approximately Lorentzian in each sample. Therefore, we use a single linewidth parameter, $\Delta H_{p\text{-}p}(T)$, the separation of the extrema of the derivative, to describe the line at temperature T. The temperature dependence observed for the component of the linewidth due to relaxation,

$$\Delta H_l(T)=\Delta H_{p\text{-}p}(T)-\Delta H_0\ , \tag{3}$$

is shown for both samples in Fig. 2 over the range $T=7-18$ K. The solid curve is $D(e^{\Delta/T}-1)^{-1}$, with $\Delta=34.3$ K and $D=7.1\times10^3$ G. For changes in Δ of 12%, the systematic excursion from the data is clearly greater than the experimental uncertainty. At temperatures above 5 K the line of inverted phase was present in the center of the $\Delta m=1$ transition but had no effect on the linewidth or the determination of the temperature-dependent linewidth $\Delta H_{p\text{-}p}(T)$. Above 10 K, where $\Delta H_{p\text{-}p}(T)$ is over 450 G, contributions from the $\Delta m=2$ transition to the low-field wing of the Lorentzian $\Delta m=1$ line makes the determination of $\Delta H_{p\text{-}p}(T)$ less precise, as reflected in the scatter in Fig. 2. The maximum the contribution from the typical Raman terms of Eq. (2) can be without introducing noticeable deviation from the data is about 25% at the highest temperature, 18 K.

DISCUSSION

The presence of a phonon-limited relaxation[23] in the one-phonon or "direct" process is experimentally distinguishable from the intrinsic (normal spin-lattice relaxation) process by four characteristic properties: (i) The recovery signal of the spins is after pulse saturation nonexponential; the recovery rate $1/\tau$ of the resonant phonons and spins to the rest of the world is taken to be the long asymptotic exponential. (ii) The temperature dependence of the recovery rate is changed from the intrinsic value of $\coth(h\nu/2kT)$ to $\coth^2(h\nu/2kT)$. In the temperature range considered here, this is from T to T^2, to a very good approximation. (iii) and (iv) The recovery rate is inversely proportional to the concentration of paramagnetic ions and to the phonon scattering length.

We have observed the nonexponential recovery, the T^2 dependence, and the inverse proportionality to Fe^{2+} concentration. We attempted to observe the phonon scattering length dependence by cleaving sample 1, reducing its smallest dimension by approximately half. Since the recovery rate did not change we conclude the phonon scattering length in this crystal to be less than 0.5 mm, consistent with its milky appearance.

The nonexponential recovery signal cannot be taken as proof of the existence of a phonon bottleneck in the $S=1$ system as it can be in the $S=\frac{1}{2}$ system, since the rate equation for the intrinsic process predicts a single exponential for $S=\frac{1}{2}$ and a double exponential for $S=1$. There are, however, two features of the intrinsic relaxation process of a three-level system that are predictable from the rate equations—the angular dependence and a change in the recovery rate at the center of the resonance line. These effects have been observed[21] in Fe^{2+} : MgO at 100 ppm. In our experiment on CaO we found no angular dependence and no change in the recovery rate at the center of the line. Based on the value of the transverse acoustic frequency in CaO found by Evans and Kemp,[24] the velocity of propagation of transverse acoustic waves v_T is approximately three-fourths of its MgO value. This fact makes the presence of a phonon bottleneck[25] in CaO at the same Fe^{2+} concentration at which the intrinsic relaxation occurs in MgO entirely reasonable.

The recovery shape of a phonon-limited three-level system has been analyzed by Brya,[26] and our measurements show qualitative agreement with this prediction. The spins initially decay at an intrinsic spin-lattice relaxation rate (this is strictly true only at the center of the resonance line where the levels are equally spaced; however, it is approximately true at saturation even where the levels are not equally spaced) after reaching equilibrium with the resonant phonons; the spin (resonant) phonon system decays to the bath temperature. At the center of the resonance line the only substantial change in the recovery signal was an increase in amplitude.

A phonon bottleneck in the direct process of a triplet spin state with strong electron-phonon coupling has been reported[26, 27] for Ni^{2+} : MgO and evidence of a 9-GHz phonon bottleneck in Fe^{2+}: MgO has been found by Shiren.[28]

A phonon bottleneck at the energy of an excited electronic state generated by an Orbach process exhibits a single exponential recovery signal after saturation by a long pulse. The same temperature dependence [Eq. (1)] is expected as for the intrinsic Orbach process. It is not clear what the effect of interference terms between two phonon processes, as suggested by Stoneham[29] for more than one excited state, might be in this case. The only expected dependence of τ in the Orbach region is the inverse concentration dependence and the crystal size dependence. Our results for the former show the inverse concentration dependence expected for a bottleneck at 23.9 cm^{-1}. The latter test was inconclusive; we attribute the absence of crystal size dependence to the same cause as in the direct region. The existence of a phonon bottleneck at comparable energy (29 cm^{-1}) and at lower concentration (10^{12}–10^{15}) has been clearly demonstrated[30] for ruby by Geschwind and coworkers.

Line broadening can be caused by shortened lifetimes, by changes in the local strain, and/or by exchange coupling. In the temperature range considered here the thermal expansion coefficient of CaO is very small, therefore, the changes in strain are probably too small to explain the data. The low concentrations, absence of temperature cycling effects, and concentration dependence argue against exchange effects. We have attributed all of the line broadening to shortened lifetimes, consistent with our model of the spin recovery, even though the other causes cannot be entirely ruled out.

We have found that the line broadening as a function of temperature is dominated by the Orbach process and is independent of the concentration of Fe^{2+} (see Fig. 2). Culvahouse and Richards have treated[31] lifetime broadening due to an Orbach process. In their discussion, they concluded that the most probable explanation of the T_1/T_2 ratios observed by Stapleton and Brower[32] in neodymium-doped yttrium ethyl sulfate, a Kramers ion, was a phonon bottleneck generated by an Orbach process. Later this speculation was experimentally verified[33] using the same experimental criteria as stated above.

An estimate of the magniutde of the T^5 Raman process for Fe^{2+} in MgO has been made by Ham.[34] Since many of the constants for the transition probability [Eq. (8) of his paper] are not available for CaO, we have used the same values for all the constants with the exception of v_T (clearly the single most important factor since it occurs to the tenth power); as stated above, v_T in CaO is approximately three-fourths the value measured in MgO. This estimate and a similar one for T^7 show the Raman processes to be a factor of $\sim 10^3$ too long to account for the measured recovery times. On the other hand, with $\Delta = 23.9$ cm^{-1}, the magnitude of the intrinsic Orbach process is estimated,[34] using Ham's equation (9) and the same constants as above, to be approximately 15 times faster than the observed recovery measured here. We consider this estimate to be additional confirmation that the observed Orbach process is bottlenecked.

The line broadening data show these estimates are essentially correct by demonstrating the dominance of the Orbach process up to $T = 15$ K. If one calculates the coefficient of the Orbach term by equating T_1 to T_2 and $1/T_2 = \pi\sqrt{3}h^{-1}g\mu_B\,\Delta H_l(T)$, appropriate for a Lorentzian line, the value obtained is also about 15 times larger than the value of B measured near 4 K. T_1 and T_2 are not expected to be equal theoretically[31] or from past experimental evidence,[35] however, they are expected to be the same order of magnitude.

CONCLUSIONS

The energy of the first excited state(s) is found to be 23.9 ± 1.5 cm^{-1} for Fe^{2+} in CaO. Comparison with the value 105 cm^{-1} for the same quantity in MgO indicates that the dynamic Jahn-Teller effect is, as proposed by Ham, the effective mechanism for this orbital reduction.

Theoretical estimates of the magnitudes of the normal Raman process(es) and the Orbach process clearly show that the spin recovery is dominated by the Orbach process. The line broadening data confirm the dominance of the Orbach process even at temperatures as high as 15 K and is consistent with the value of the first excited energy level(s) obtained from recovery data.

In CaO, we find that recovery of Fe^{2+} spins from pulse saturation in applied fields of about 1880 G generates a severe phonon bottleneck at ion concentration of 100 ppm and at sample temperatures from 1.3 to 2.2 K. In this "direct" region, the phonon bottleneck involves heating of 8.9- and 17.8-GHz phonons.

At temperatures from 2.5 to 4.2 K, we have observed relaxation via excited states. The concentration dependence of the coefficient of this Orbach process shows that a phonon bottleneck is also generated at 717 GHz.

The presence of phonon bottlenecks for Fe^{2+} at 100 ppm in CaO is consistent with the previous observation of intrinsic relaxation for the same concentrations of Fe^{2+} in MgO since v_T in CaO is about three-fourths that in MgO.

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[1] K. W. H. Stevens, Proc. Roy. Soc. (London) A219, 542 (1953).

[2] A. J. Shushus, J. Chem. Phys. 40, 1602 (1964).

[3] W. Low, Phys. Rev. 101, 1827 (1956).

[4] W. Low and M. Weger, Phys. Rev. 118, 1130 (1960).

[5] F. S. Ham, W. M. Schwarz, and Mary C. M. O'Brien, Phys. Rev. 185, 548 (1969).

[6] J. Chappert, R. B. Frankel, and N. A. Blum, Phys. Letters 25A, 149 (1967).

[7] Frank S. Ham, Phys. Rev. 138, 1727 (1965).

[8] M. D. Sturge, *Solid State Physics* (Academic, New York, 1967), Vol. 20.

[9] J. Y. Wong, Phys. Rev. 168, 337 (1968).

[10] E. L. Wilkinson, R. L. Hartman, and J. G. Castle, Jr., Phys. Rev. 171, 299 (1968).

[11] R. H. Dicke and R. H. Romer, Rev. Sci. Instr. 26, 915 (1955).

[12] R. L. Hartman, J. S. Bennett, and J. G. Castle, Jr., Phys. Rev. B 1, 1946 (1970).

[13] D. W. Feldman and J. G. Castle, Jr., Phys. Rev. 121, 1349 (1961).

[14] Thermax is the trademark of Commercial Solvents Corp., New York, N. Y.

[15] R. L. Hartman, J. S. Bennett, and R. A. Jensen, Bull. Am. Phys. Soc. 13, 244 (1968).

[16] J. S. Bennett, U. S. Army Missile Command Report No. RR-TR-69-13, 1969 (unpublished).

[17] Waveform Eductor is the trademark of Princeton Applied Research, Princeton, N. J.

[18] E. H. Shulte, Cryogenics 6, 321 (1966).

[19] J. R. Clements and E. H. Quinell, Rev. Sci. Instr. 23, 213 (1952).

[20] Stephen R. P. Smith, Fricis Dravnieks, and John E. Wertz, Phys. Rev. 178, 471 (1969).

[21] M. F. Lewis and A. M. Stoneham, Phys. Rev. 164, 271 (1967).

[22] We use the definition which related the standard deviation to the width of the distribution.

[23] For a discussion of the proper choice of the Debye temperature, see J. G. Castle, Jr., in *Localized Excitations in Solids* (Plenum, New York, 1968), p. 388.

[24] Bruce D. Evans and James C. Kemp, Phys. Rev. B 2, 4179 (1970).

[25] J. H. Van Vleck, Phys. Rev. 59, 724 (1941).

[26] W. J. Brya, Phys. Rev. B 3, 635 (1971).

[27] N. S. Shiren, in *Proceedings of the Fourteenth Colloque Ampere, Ljubljana*, 1966 (North-Holland, Amsterdam, 1967), p. 213.

[28] N. S. Shiren, Phys. Rev. Letters 17, 958 (1966).

[29] A. M. Stoneham, Phys. Status Solidi 19, 787 (1967).

[30] R. Adde, S. Geschwind, and L. R. Walker, *Colloque Ampere XV* (North-Holland, Amsterdam, 1969), p. 460.

[31] J. W. Culvahouse and Peter M. Richards, Phys. Rev. 178, 485 (1969).

[32] H. J. Stapleton and K. L. Brower, Phys. Rev. 178, 481 (1969).

[33] Gh. Cristea, T. L. Bahan, and H. J. Stapleton, Phys. Rev. B 4, 2081 (1971).

[34] Frank S. Ham, Phys. Rev. 160, 328 (1967).

[35] R. L. Hartman and J. S. Bennett, Bull. Am. Phys. Soc. 13, 1700 (1968).