PHYSICAL REVIEW B VOLUME 6, NUMBER 5 1 SEPTEMBER 1972

Spin-Lattice Relaxation-Time Measurements of Trivalent Iron in Single-Crystal Calcite[†]

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(Received 22 February 1972)

The spin-lattice relaxation time for the $M=-\frac{1}{2}\rightarrow\frac{1}{2}$ transition of trivalent iron in single-crystal calcite has been measured at X band by pulse recovery from 1.4 to 45 K and by spectral line broadening from 40 to 195 K. The resulting transition-probability data are well described by the sum of a direct-process term and a Raman-process term, the latter having a T^5 dependence in its low-temperature regime. An effective Debye temperature of $\Theta = 463 \pm 5$ K is obtained as a best-fit parameter for the Raman process.

I. INTRODUCTION

It has been pointed out that in the case of a Kramers ion whose ground term is a well-isolated orbital singlet with a spin multiplicity greater than 2, the Raman-process contribution to the spin-lattice relaxation will operate through intermediate spin states from within the ground term.[1] Consequently, the spin-lattice relaxation transition probability should be proportional to T^5 at low temperatures.[2,3] The first reported example of such a temperature dependence is that given by Pashinin and Prokhorov[4] for the case of iron in $K_3Co(CN)_6$. Similar results have been reported for other ions of the $3d$ and $4f$ series in various hosts.[5–12] The purpose of this report is to present data on the spin-lattice relaxation time of trivalent iron in calcite, which is a system exhibiting such a T^5 dependence of the relaxation probability in the low-temperature regime of the Raman process.

The iron impurities which give rise to this electron-spin-resonance (ESR) absorption spectrum in single-crystal calcite ($CaCO_3$) are located as substitutions at the two crystallographically nonequivalent calcium ion sites.[13] Just as in the case of divalent manganese,[14] there are two nonequivalent sets of iron ions, these being related to each other by an improper rotation. Under the action of the local C_{3v} symmetry, the sixfold spin-degenerate ^6S ground term of trivalent iron is split into three Kramers doublets.[13] In the high magnetic field limit, two sets of five ESR transitions will generally be observable. With the magnetic field directed along the crystal c axis, these two sets become degenerate, as required by symmetry.

An important property of calcite is the small degree of nuclear magnetism. (The only nonzero spin nucleus of significant abundance in calcite is ^{13}C whose natural abundance is 1.1%.) Another property of calcite is its relatively high degree of crystalline perfection. One consequence of these properties of calcite is the rather narrow ESR absorption lines observed in the spectra of various free-radical species and atomic ions. For example, the $M=-\frac{1}{2}\rightarrow\frac{1}{2}$ spectral component of trivalent iron in this host is 0.025 Oe at 18 K (see Table I). Several benefits accrue from such relatively narrow spectral lines. The most important of these are as follows: (a) Relaxation-time measurements may be made from spectral lines having relatively low total intensities, (b) effects due to concentration may be commensurately reduced, and (c) cross relaxation will be less probable due to the reduction of overlap in the wings of spectral line components and the absence of unresolved hyperfine structure.

It is for these reasons that an investigation has been undertaken on the spin-lattice relaxation time vs temperature for this crystal-ion system. Owing to the rather uncomplicated nature of the ESR spectrum, the interpretation of the results appears to be in reasonable agreement with existing theories.

II. EXPERIMENT

The spectrometer used in this investigation operated at X band and employed a 30-MHz superheterodyne detector having a 1-MHz-bandwidth intermediate-frequency amplifier. Frequency of the signal klystron was stabilized to within 1 part in 10^8 for periods of the order of 1 h by phase locking to X-band harmonics from a quartz-crystal-controlled oscillator. Fine tuning was provided so that the signal frequency could be trimmed to the peak of the absorption response function of the specimen cavity resonator. For both pulse-recovery and line-broadening measurements, a gas-tight cylindrical-cavity resonator operating in the

TABLE I. Representative linewidth data vs temperature for the $M = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition of trivalent iron in single-crystal calcite for the magnetic field directed along the crystal c axis. The trivalent-iron ion concentration is estimated at 5 ppm by weight.

Temperature (K)	Linewidth[a] (Oe)
4.2	0.052
18	0.025
34	0.025
77	0.115
115	0.396
165	1.06
195	1.78

[a] The uncertainty in these measurements is of the order of 5%.

TE_{011} mode was employed. In general, Q factors of the order of 5000 were obtained. All relaxation times were obtained at magnetic fields of the order of 3400 Oe.

Three types of thermometers were used to determine temperature. From 1.25 to 2.00 K a U-tube manometer containing butyl pthalate was used. Between 2.00 and 4.2 K, use was made of an aneroid manometer. Both manometers measured pressure above the liquid-helium bath and temperature was established by making use of conversion tables.[15] Above 4.2 K two calibrated resistance thermometers were employed. These were buried within a brass section of the cavity resonator with thermal contact assisted by silicone grease. The range from 4.2 to 20 K was covered by a carbon-composition resistor and from 15 to 200 K an annealed platinum-wire resistor was used.

Above the liquid-helium range, temperature was controlled by transferring cold helium gas to the vacuum bottle containing the specimen cavity resonator. This gas was produced by dissipating electrical power from a resistance element held at the bottom of the liquid-helium storage bottle. The transfer rate of helium gas was adjusted by varying the power delivered to the resistance element. This method of controlling temperature above the liquid-helium range is essentially that described by Kiel and Mims.[16]

In the pulse-recovery method of making relaxation-time measurements, two sets of adjustable microwave diode attenuators were employed, each having a maximum attenuation of 60 dB. One set was placed in the microwave path leading to the specimen cavity resonator and the other was placed immediately before the superheterodyne mixer. These two sets of attenuators were switched in such a manner as to have their relative on-off sequences out of phase by 180 deg. In this manner, power to the specimen cavity resonator could be altered while at the same time maintaining a nearly constant level of microwave power at the superheterodyne mixer.[17]

Above 40 K relaxation times were obtained from linewidth measurements. For such measurements a procedure was adopted which was designed to reduce the chance of observational errors and to semi-automate the process of determining linewidths. The first step in this procedure consisted of processing an ESR signal through a phase-sensitive lock-in–type detector and then adjusting the magnetic field to a value corresponding to an inflection point of the ESR absorption. The strength of this magnetic field was obtained from an NMR spectrometer of the Pound-Watkins type.[18] The detected output of this spectrometer was fed to a second phase-sensitive lock-in–type detector whose output was used to drive a voltage-dependent capacitor in the tank circuit of the NMR spectrometer. By proper choice of phase, the frequency of the NMR spectrometer could be held to that required for proton resonance. This frequency was read from an electronic counter. In this manner linewidths could be determined by repeating the process for the other inflection point of the ESR absorption.

For this investigation single crystals were cut from calcite rhombohedra into parallelepipeds of dimensions 5×5×15 mm. All specimens were of optical quality and exhibited ESR spectra of trivalent iron and of divalent manganese; slight variations were observed in the total intensities of the spectra of iron and manganese. Some pulse-recovery measurements were made on (a) specimens of differing surface-area-to-volume ratios and (b) specimens which were in direct contact with the liquid-helium bath. In all cases, a single exponential recovery was observed and at a given temperature the relaxation time was unique to within measurement errors. All the specimens studied had, to within 25%, the same concentration of trivalent iron—5 ppm.

In the temperature range ($T > 40$ K) where the shortening of the spin-lattice-interaction lifetime sensibly contributes to spectral line broadening, the relaxation rate is taken to be[19,20]

$$\tau^{-1} = (g\mu_B/\hbar)\,\Delta H_e, \tag{1}$$

where ΔH_e is the contribution to the spectral linewidth due to relaxation-interaction lifetime shortening. For Gaussian-shape factors the relation between the total linewidth ΔH_t, the residual or temperature-independent linewdith ΔH_0, and ΔH_e is given by[21–23]

$$(\Delta H_t)^2 = (\Delta H_0)^2 + (\Delta H_e)^2. \tag{2}$$

Although it has been stressed that certain properties of calcite operate to permit rather narrow ESR absorption lines, some residual effects are still present and tend to cause spectral lines to assume shapes which are intermediate to Lorentzian and Gaussian. These are unresolved and partially resolved superhyperfine structure due to ^{13}C, some unavoidable strain, magnetic field inhomogeneity, and crystalline mosaic whose effects are not totally absent for the $M=-\frac{1}{2}\rightarrow\frac{1}{2}$ transition of trivalent iron.[24] In the highest-temperature region of these relaxation-time measurements, the ESR absorptions broadened sufficiently to become Lorentzian in shape. For this case there is no detectable difference between using ΔH_t for the effective linewidth or ΔH_e since the latter overwhelms ΔH_0.[25,26] The justification for using the expression given in Eq. (2) to determine relaxation times was established by corroborating the pulse-recovery data with linewidth data in the temperature range 40–45 K.[27,28] These two methods gave results which were identical to within measurement error.

III. RESULTS AND DISCUSSION

The spin-lattice relaxation-time results for the $M=-\frac{1}{2}\rightarrow\frac{1}{2}$ transition of trivalent iron in calcite, with the magnetic field directed along the c axis, are shown in Fig. 1. These data were obtained by pulse recovery from 1.25 to 45 K and by spectral line broadening from 40 to 195 K. [Attempts to make similar measurements on other transitions or at other orientations proved to be unproductive due to excessive linewidths (see Ref. 11).] The over-all temperature dependence of the spin-lattice relaxation probability is given by

$$\tau^{-1}=AT+BJ_4(\alpha), \qquad (3)$$

where $A=0.110\times10^2$ sec^{-1} K^{-1}, $B=0.693\times10^9$ sec^{-1}, $\alpha=\Theta/T$, $\Theta=463\pm5$ K, and $J_n(\alpha)$ is the modified Raman integral of order n defined as[29,30]

$$J_n(\alpha)=\frac{1}{(\alpha)^{n+1}}\int_0^{\alpha}\frac{x^n\,dx}{(e^x-1)(1-e^{-x})}\,. \qquad (4)$$

In first order, S-state ions will not have their spin degeneracy lifted by a crystalline electric field. Consequently, such degeneracy removal, as well as spin-lattice interaction, will in general be small. This is observed to be the case for this crystal-ion system. Below 40 K the temperature dependence of the spin-lattice relaxation rate is well approximated by

$$\tau^{-1}=AT+B'T^5, \qquad (5)$$

where $B'=0.84\times10^{-3}$ sec^{-1} K^{-5}. These values of A and B' appear to be contained within the range of such coefficients found for other S-state ions in cubic hosts.[5-7] For the present case, the coefficient B' may be approximated by[25]

$$B'=(54k^5/\rho^2v^{10}\hbar^7\pi^3)V^4, \qquad (6)$$

where ρ is density, v is the velocity of sound, and V is a certain product of matrix elements which connect the $M=\pm\frac{1}{2}$ states to other spin states of the ^6S manifold ground term of trivalent iron. Since it is difficult to obtain V from first principles, Eq. (6) may be turned around to yield an estimate for V. Using the mean value for the velocity of sound in calcite,[31] the value $V=88$ cm^{-1} is obtained by this procedure. This is larger than the corresponding values for rare-earth S-state ions[5-7] and is of the same order as for divalent manganese in BaF$_2$ and SrF$_2$.[7]

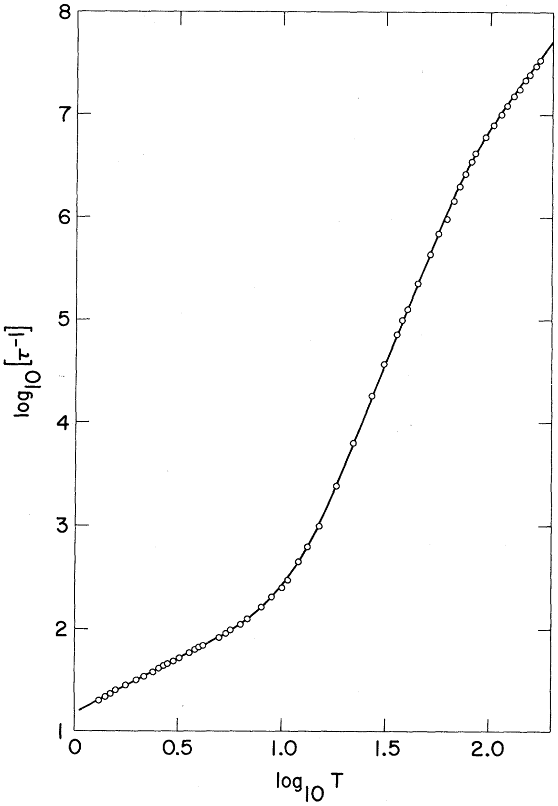

FIG. 1. Spin-lattice relaxation-probability data as function of temperature. Each point represents the mean value of a least 5 measurements. Over the entire temperature range, the uncertainties in the measurements do not exceed 5%. The solid curve is derived from the equation $\tau^{-1}=AT+BJ_4(\alpha)$, where $A=0.110\times10^2$ sec^{-1} K^{-1}, $B=0.693\times10^9$ sec^{-1}, $\alpha=\Theta/T$, and $\Theta=463$ K.

As a consequence of the relatively low uncertainties in the relaxation-time measurements, the effective Debye temperature has been determined, within the order of 1%, to be 463 K. This is to be compared with the value $\Theta=210.6$ K obtained by low-temperature specific-heat measurements[32,33] and the value $\Theta=469$ K obtained from elastic-constant data taken at room temperature.[34] It is interesting to note that the value of Θ obtained here agrees closely with that obtained from elastic-constant results and yet is more than twice the Debye temperature obtained from low-temperature specific-heat measurements. These are, of course, three different phenomena and, although they may be connected through related interaction mechanisms involving the lattice, each must be taken as an idealized approximation if meaningful calculations are to be provided. One such approximation is the Debye model of the solid. In the case of calcite such an approximation could lead to difficulties which arise from the internal vibrations of the carbonate ion. The high value of the effective Debye temperatures obtained here may, in fact, be a reflection of this possible phenomenon. That is, excitation of high-frequency modes due to molecular-vibration states and modes in the optical branch could combine to yield this average effective Debye temperature.

Finally, it should be noted from the linewidth measurements (see Table I) that an unusual line-broadening process sets in at temperatures below 18 K. No interpretation of this phenomenon is given here.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Wm. B. McConnaughey for his valuable assistance in obtaining spectral linewidth data. One of us (S.V.N.) would like to thank both the State Committee for Nuclear Energy of Rumania and the U. S. National Science Foundation for financial support during the period of this research and the U. S. Atomic Energy Commission, under whose auspices this work was performed.

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†Work performed under the auspices of the U. S. Atomic Energy Commission.

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