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Spin Relaxation via Low-Lying Energy Level of Fe^{2+} in MgO

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The spin-relaxation time (T_1) of Fe^{2+} in MgO was measured from 4.2 to 13°K. The excess relaxation above that attributed to the direct processes dominant at low temperature is described by $1/T_1 = Ae^{-\Delta/T}$, where $A = 6.5\times10^{10}$ sec^{-1} and $\Delta = 140$°K. This result establishes, via a measurement of the Orbach process, that there is a sharp electronic energy level at 100 ± 10 cm^{-1} for the Fe^{2+} ion in MgO.

I. INTRODUCTION

THE spin relaxation of Fe^{2+} in MgO has been known[1,2] to be fast compared with other ions in the same host,[3–5] indicating a strong electron-phonon interaction.[6,7] Mössbauer studies led to a recent prediction[8] that there is an excited electronic state of Fe^{2+}:MgO whose energy is lower than predicted by crystal-field theory. We therefore measured the temperature dependence of the spin relaxation at higher temperatures in order to determine the energy of this electronic state of the Fe^{2+}:MgO complex.

II. EXPERIMENTAL

Measurements were made on three samples which varied in Fe^{2+} concentration and in treatment. Both the linewidth and the relaxation time (T_1) at 4.2°K varied between samples, but T_1 at each temperature above 8°K was the same in each sample. The sample for which the results are presented in Sec. II had the narrowest line (~400 G) and slowest T_1 at 4.2°K. In practice, this means that this sample afforded the largest signals and the greatest range of data. The sample initially contained about 0.01% Fe^{3+} and negligible Fe^{2+}, as estimated from the electron-paramagnetic-resonance (EPR) signals. The sample was heated to 1300°C at 10^{-6} Torr, resulting in a greater than 90% decrease of the Fe^{3+} signal. We therefore estimate the Fe^{2+} concentration of the sample to be about 0.01%.[9] Rapid quenching from high temperature had resulted in wide lines; the 400-G width was achieved when this sample was cooled from 1300°C over 10 h. The sample also contained about 0.01% Cr and Mn, but since these relax more slowly at the same temperature they are not expected to influence the result.

The EPR spectrum of the ground-state triplet of Fe^{2+} in MgO consists of a $\Delta M = 2$ transition, a $\Delta M = 1$ transition at $g = 3.5$, and a sharp two-quantum transition superimposed on the $\Delta M = 1$ line.[10] The data were taken at $g = 3.5$, with a frequency of 9.1 GHz and a magnetic field of 1870 G. The resonance absorption was saturated with 10 mW of pulse power, and monitored with 1 μW of power. The relaxation above 8°K was observed to be a single exponent, and at each temperature T_1 was found to be independent of pulse power, pulse width, and monitor power.

The data were taken by the pulse-saturation method employing a traveling-wave-tube (TWT) spectrometer.[11] The instrument can be used to measure T_1 as fast as 0.5 μsec. The temperature was measured by vapor pressure of He and by a 270-Ω carbon resistor[12] calibrated at 2.0, 4.2, and 21.2°K, and fitted to a semi-empirical equation.[13] Relaxation signals were extracted with the aid of a wave-form eductor and a logarithmic converter. The eductor increases the signal to noise by averaging many repetitions of the signal in 100 time-sequenced channels. The fastest scan is 1 μsec/channel, limiting the use of the instrument to T_1 slower than 5 μsec. The theoretical improvement in signal to noise (square root of the number of repetitions) is about 100; in practice, the improvement was limited to a factor of 10 by lack of a suitable preamplifier. Prior to the use of the eductor the relaxation times deduced were scattered by a factor of 2; this scatter was reduced to 10% by the eductor. The memory of the eductor was slowly read out through a logarithmic converter which changed the exponential decay to a straight line

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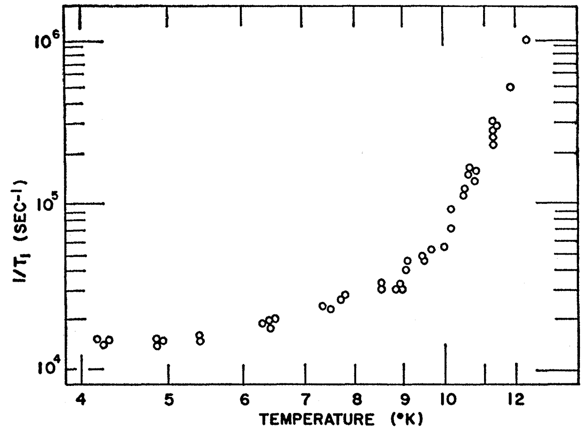

FIG. 1. Spin-lattice relaxation time T_1 of Fe^{2+} in MgO. Frequency was 9.1 GHz and field 1875 G.

whose slope was the time constant. The two relaxation points faster than 5 μsec were photographed from an oscilloscope and plotted on semilogarithmic paper.

III. RESULTS

The relaxation times observed from 4 to 13°K are plotted in Fig. 1. Figure 2 is a plot of the difference between the total relaxation rate $(1/T_1)$ and an extrapolation of the low-temperature processes approximated by $1/T_{1e}=2.8\times10^3\,T(\text{sec}^{-1}\,{}^\circ\text{K}^{-1})$. The linearity of the data when plotted in this manner shows that the relaxation above 8°K can be described by the equation

$$1/T_{10}=Ae^{-\Delta/T}, \qquad (1)$$

with $A=6.5\times10^{10}$ sec^{-1} and $\Delta=(140\pm14)$°K.[14] This characteristic temperature corresponding to the energy of 100 cm^{-1} will be discussed below as being the energy of the excited state(s) of the Fe^{2+} in MgO complex.

The temperature range over which the pulse-saturation measurement of the exponential process is possible is limited by fast relaxation at high temperatures, and by the dominance of a fast direct process at low temperatures. Extension of the range by the technique of line broadening is difficult because of the very wide lines and weak signals. However, the resonance absorption was observed at 32°K, but not at 44°K. Lifetime broadening at these temperatures would be expected to be (within a factor of 2) 30 and 4000 G, respectively, if the values of Eq. (1) are valid. Although the pulse-saturation data can be explained[15] by a combination of an Orbach process assuming $\Delta=200$°K, with a large contribution ($\sim10^3$ higher than expected on the basis of the known strain parameters[8]) from a Raman process, the line should have broadened beyond detectability (to about 1600 G) by 32°K if that explanation were valid.

IV. DISCUSSION

The low density of the Fe^{2+} ions in the sample used ($\sim$100 ppm) minimizes cooperative effects[16] and allows assignment of the relaxation to processes associated with isolated Fe^{2+} ions. Further, the multiple-exponent recoveries observed below 8°K are consistent with those expected[17] for the direct relaxation processes within the $S=1$ ground state of Fe^{2+} in MgO. The exponential form of Eq. (1) is indicative of a phonon-relaxation process involving an excited electronic state[18] and the Δ in this expression is characteristic of the energy of that excited level, under the valid assumption that $\Delta\gg T$. This value of Δ agrees with the energy spacing of an infrared absorption[19] in the same material. Our results are not as precise as the infrared results but do confirm the assignment of the 100-cm^{-1} line to a transition involving the Γ_{5g} ground state of the Fe^{2+} ion. This value of Δ is also consistent with that predicted[8] to explain Mössbauer data[20] concerning this ion. Although our result for Δ is lower than the crystal-field-theory prediction,[10] Ham[8] has pointed out that both covalent bonding and Jahn-Teller distortion could reasonably be expected to reduce Δ to the observed value of 100 cm^{-1}.

V. CONCLUSION

Above 8°K the spin relaxation of Fe^{2+} in MgO is dominated by the electron-lattice interaction via one

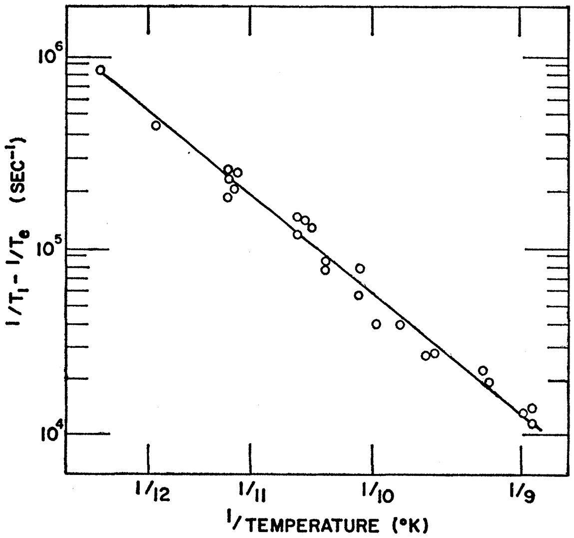

FIG. 2. Relaxation of Fe^{2+} in MgO. Plotted values are the difference between $1/T_1$ measured and $1/T_{1e}$, the extrapolated values of the low-temperature process.

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Role of Electronic Structure in Determining the Charges of Fast Ions in Matter*

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Some equilibrium charge-state distributions of $7\text{–}11\times10^8$ cm/sec ^{10}B, ^{12}C, and ^{13}C ions in plastic films and in carbon have been determined by spectrometry of the recoils from the ^{12}C(d, α), ^{12}C(d, d'), and ^{12}C(d, p) reactions at 15 MeV. A simple phenomenological model is presented for the capture and loss of electrons in a beam at charge-state equilibrium. The present experimental results, together with all previously published data on the equilibrium charge states in plastics of ions in the second period of the periodic table, are analyzed within the framework of the model for the influence of the electronic structure of the ions. A universal correlation with the respective ionization potentials is found when the "same" electrons are compared in all ions. Indications are that the same kind of correlation prevails also in heavier ions. The model and its resultant correlations focus upon the equality of capture and loss cross sections as the "stripping" criterion for each electron.

I. INTRODUCTION

Studies of the charges borne by beams of ions traversing matter at velocities $\gtrsim 10^8$ cm/sec have in recent years taken on increasing interest. One reason is that the question of charge is an important one in the development of theories for the energy loss of energetic ions in matter. While existing energy-loss theory is quite accurate at velocities above $\sim10^9$ cm/sec where the ions are completely stripped of atomic electrons, the development of an adequate energy-loss theory for partially stripped ions has been hindered partly by a lack of knowledge of how the ionic charge depends on velocity and other variables. A more practical reason for the current interest in charge-state studies is the fact that heavy-ion accelerator technology is in need of guidance concerning the most efficient methods of stripping ions to a given charge for acceleration.

The variable which is most influential in determining the charge population of a beam of ions which has traversed a given amount of matter is the velocity of of the ions. The charge distribution at a given velocity v can be specified either by stating the fractions ϕ_i of the beam that are in the various charge states i $(0\leqslant i\leqslant Z)$ or, more coarsely, by stating the mean charge $\bar{\imath}$ of the beam: $\bar{\imath}=\sum i\phi_i$. Abundance curves, i.e., families of curves showing ϕ_i versus v for all charge states, each in succession rising and falling as the velocity varies, are the most detailed and, as will be pointed out below, phenomenologically significant method of displaying charge-versus-velocity data. Useful for practical applications, however, are mean-charge curves: plots of $\bar{\imath}$ versus v. Complete mean-charge curves have been obtained only for a few light ions. They appear to be smooth and asymptotic to $\bar{\imath}=Z$ at high velocities.

A second variable which influences the charge population of a beam of ions is the amount of matter through which it has passed. As a beam of given velocity and arbitrary charge-state distribution enters a medium, the distribution changes with penetration distance until a certain minimum thickness has been traversed, after which it remains constant as the so-called equilibrium charge-state distribution. While the constancy of the equilibrium charge-state distribution may upon closer examination have to be questioned, it appears at present to be a useful way to characterize a beam of ions of a given identity at a given velocity.

The nature of the equilibration medium has been found to have a measurable effect on the equilibrium distribution. For example, solid media appear to produce, in general, higher-charge states than do gaseous media. In one recent study,[1] a gas of complex molecular structure (naphthalene) has been found to produce higher-charge states in carbon ions than does one of simpler molecular structure (iodine). This third variable, the nature of the equilibration medium, has not

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