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Field-Dependent Spin-Lattice Relaxation of Cr^{3+} in Al_2O_3

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The variation of spin-lattice relaxation time (T_1) with magnetic field (B) for the Cr^{3+} ion in ruby has been measured under non-Kramers conditions for fields between 0.3 and 2.6 tesla, corresponding to microwave frequencies in the range 9 to 71 GHz. Below about 0.8 tesla there is a slow variation, approximately as $T_1 \propto B^{-0.4}$; at higher fields the variation becomes more rapid, approaching $T_1 \propto B^{-2.0}$ at 2.6 tesla. This behaviour is explained in terms of the non-linear divergence of the energy levels with field.

1. Introduction

Previous authors have estimated the effect of a magnetic field on the spin-lattice relaxation of Cr^{3+} in ruby by attempting to collate results obtained by several workers. This approach led Donoho [1] to conclude that, in ruby, there was very little field dependence up to fields of about 1.3 tesla, corresponding to microwave frequencies in the 35 GHz range. However, single ion theory [2-4], shows that, in general, the spin-lattice relaxation time should be field-dependent at low temperatures in the direct region of relaxation, the detailed variation being governed by the nature of the ion involved. Two particular cases arise, (a) the ion represented by an isolated Kramers doublet, and (b) the non-Kramers ion. The former case has already been studied [2], and theory predicts a variation inversely proportional to the fourth power of the magnetic field. Close agreement with this was found by Davids and Wagner [5] for Fe^{3+} in potassium colbalticyanide, a material possessing an isolated Kramers doublet. Although Cr^{3+} ($3d^3$) in ruby has a $4F_{3/2}$ ground state consisting of two Kramers doublets, transitions are possible between the doublets and these are not governed by Kramers' theorem. For non-Kramers ions, theory shows that the relaxation time depends inversely upon the square of the separation of the energy levels. When the zero-field splitting is very much less than the level separation, $\delta_{ab'}$, and δ_{ab} is directly proportional to the applied magnetic field, the relaxation time will vary inversely as the square of the magnetic field.

The present work was undertaken to compare experiment with theory for non-Kramers conditions, under which most of the previous experimental data had been obtained. A drawback in utilising collected results from various workers lies in the difficulty of taking account of possible differences in samples or techniques, and of factors such as chromium concentration, chemical purity, valence state and crystalline quality, all of which have been shown recently [6] to be capable of exerting considerable influence on relaxation behaviour. In an attempt to overcome these difficulties the field dependence in ruby has now been studied by observing the behaviour of specially selected crystals in a series of spectrometers operating with magnetic fields of up to 2.6 tesla.

2. Experimental

The samples selected for this work were chosen from those which had previously been used in studies of the influence of crystalline imperfection on spin-lattice relaxation [7] and on inhomogeneous line broadening [8]; consequently information about their purity, concentration and perfection was known. In particular, three conditions were fulfilled: (a) the chemical purity was high, there being only trace-level proportions of Fe^{3+} present and no detectable ionic state of chromium other than Cr^{3+}; (b) the chromium concentrations were all less than 0.05 at. %, i.e. well within the range over which Standley and Vaughan [9] have demonstrated that relaxation rates in the direct region are concentration-independent; (c) there was no evidence in the microwave spectra of any of the samples of the presence of absorption lines due to Cr^{3+} ion pairs [10]. Consequently the results could be regarded as characterising the behaviour of single Cr^{3+} ions.

The measurements of relaxation time, T_1, were made at 4.2 K, with spectrometers operating at 9.3, 16, 22, 35.5 and 71 GHz respectively. These enabled T_1 to be measured for each sample at several field values in the range between 0.3 and 2.6 tesla. Depending on the availability of components, either pulse saturation or pulse response techniques were adopted; these techniques have been reported previously [11, 12], and have been shown to give identical relaxation times. The 2-3 transition was studied at a polar angle θ of 90° (fig. 1). The energy levels of Cr^{3+} constitute a multi-level system and the relaxation behaviour of the pair of levels being monitored may be modified by the relaxation constants appropriate to the other pairs of levels in the system. These amplitude constants have been evaluated by Donoho [1] and at a polar angle of 90° one constant is of large amplitude while the others are relatively small. The relaxation behaviour at this polar angle is predominantly that of a single pair of levels and so presents the simplest case for study.

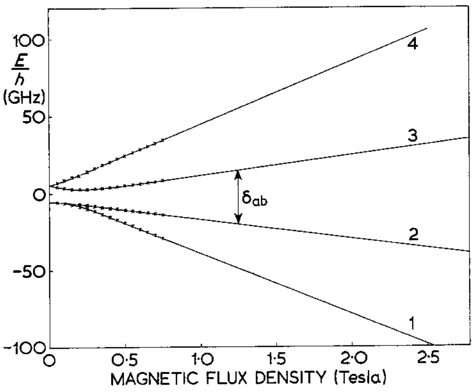

Figure 1 Ruby energy levels, $\theta = 90°$.

3. Results

3.1. Measurements on Individual Crystals

Fig. 2 shows the type of variation of T_1 with magnetic field found for a ruby having a chromium concentration of 0.041 at. %. The full lines give the results for the 2-3 transition at a polar angle of 90°, the temperature being 4.2 K. For the same orientation and transition, closely similar results were obtained with other samples whose concentrations were less than 0.05 at. %. It appears from the figure that the field dependence is considerably less rapid in the lower field region (below about 0.8 tesla) than in the higher field region and in these regions, least mean square straight lines have been drawn on the log-log plot. The slopes of these lines yield estimates of the exponents of B in each region, though in the high field region the estimate is approximate since the limited experimental data for the highest fields provides insufficient evidence to show whether the rate of change has yet become constant. In the example of fig. 2 the values of the exponents of B are -0.4 and -2.0 for the low and high field regions respectively. These values, together with those obtained for some other crystals, are given in table I.

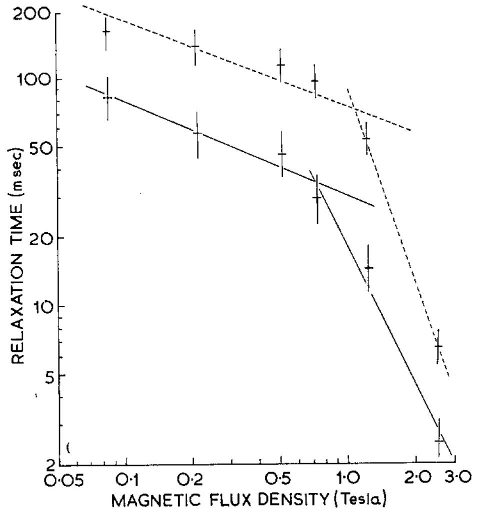

Figure 2 Dependence of T_1 and $(T_1)_u$ on magnetic field. ($\theta = 90°$ transition 2-3, $T = 4.2$ K). Full line, variation of T_1. Dotted line, variation of $(T_1)_u$.

3.2. Correction for Crystalline Imperfection

The degree of crystalline imperfection in the ruby samples used had been investigated during previous studies of the influence of imperfections on relaxation behaviour [7]. Subsequently, analysis of the broadened esr linewidths obtained with the same crystals had enabled the static strain components (ϵ_{xx}, ϵ_{zz} and ϵ_{xz}) to be

TABLE I

Sample	G2A	312B	L2	337C
Growth method	Vapour phase	Vapour phase	Czochralski	Vapour phase
Concentration Cr^{3+} (at. %)	0.032	0.041	0.045	0.052
Mean *c*-axis misorientation (min.)	74	71	< 15	36
Strain components				
$-\epsilon_{xx} \times 10^4$	171	138	86	129
$-\epsilon_{zz} \times 10^4$	140	113	80	106
Field exponent at 90°, low field region, transition 2-3	0.4	0.4	0.4	0.4
Field exponent at 90°, high field region, transition 2-3	2.2	2.0	2.1	2.2

evaluated for each crystal [8]. A previous conclusion was that the spin-lattice relaxation time decreased with increasing imperfection [7]. In the following discussion the experimentally-observed relaxation time is designated T_1 and represents the value of the relaxation time in the strained crystal.

Using the values of T_1 measured on a particular spectrometer for every sample, it was possible, with the strain data available, to plot T_1 versus strain for each magnetic field value. The method is illustrated by fig. 3 which shows the results of measurements at 9.3 and 22 GHz. Here the abscissa is the total compressive strain, ϵ, taken as the vector sum of the components ϵ_{xx} and ϵ_{zz} determined previously. Each sample thus yielded, at any one frequency of measurement, one pair of values of T_1 and ϵ.

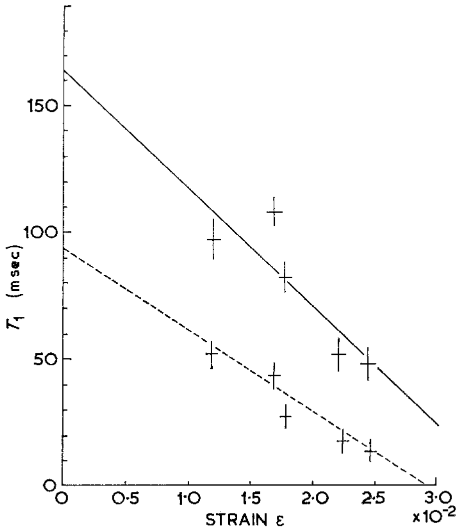

Figure 3 The variation of T_1 with strain. Full line, transition 2-3, $T = 4.2$ K, 9.3 GHz. Dotted line, transition 2-3, $T = 4.2$ K, 22 GHz.

The relaxation time T_1 decreases approximately linearly with increasing strain. For a strained crystal, in which an isotropic strain ϵ is assumed to displace the ligand ions along their radius vectors, the spin Hamiltonian will include terms of the form

$$V_0 \sum_n (1 + \epsilon)^{-(n+1)}$$

where V_0 is the static part of the crystalline potential and n is the degree of the normalised spherical harmonic Y_n^m of the angular position of the ligand ion with respect to the paramagnetic nucleus [13-15]. The expression for transition probability will also include terms of this kind. For small values of strain, the exponential expansion can be truncated and the additional term becomes linear in strain so that

$$T_1 = (T_1)_u (1 + k\epsilon) , \qquad (1)$$

where $(T_1)_u$ represents the relaxation time in unstrained material and k is a numerical constant. With compressive strain ϵ is negative. Thus, in a given magnetic field, for which there is a certain, constant, value of $(T_1)_u$ the value of T_1 should decrease linearly with increasing strain. The slope of the T_1 versus ϵ plot depends on $(T_1)_u$ and hence alters for measurements made in different values of magnetic field, due to the field dependence of $(T_1)_u$.

Using all the data from graphs similar to fig. 3, the values of $(T_1)_u$ were obtained for each value of magnetic field. These values were then plotted against field, as shown by the dotted lines in fig. 2. Again, the results refer to measurements made at 4.2 K in the direct region of relaxation. In the low and high field regions the slopes of the lines give exponents of B of -0.4 and

−2.5 respectively. These values are similar to those given in table I indicating that the presence of strain does not appreciably affect the field dependence.

4. Discussion

The energy level diagram of Cr^{3+} in Al_2O_3 (fig. 1), is characterised by the two Kramers doublets separated, in zero magnetic field, by 11.46 GHz. This zero-field splitting is due to the small trigonal distortion (at the Cr^{3+} ion) of the crystal field symmetry, the octahedral component of which is responsible for the splitting of the orbital levels. All the experimental data were obtained for the 2-3 transition at $\theta = 90°$. The averages of the observed exponents were −0.4 and −2.1 in the low and high field regions respectively.

Consideration of fig. 1 shows that in the low field region the major part of the separation δ_{ab} between the levels concerned is due to the zero-field splitting. Following Orbach's method and notation [16], the net transition probability is

$$w = \frac{3[(\delta_{ab})/\hbar]^3}{2\pi\rho v^5\hbar} \cdot |\langle a|V_{cf}^{(1)}|b\rangle|^2 \cdot [(N_{\delta_{ab}} + 1) \, . \, N_b - N_{\delta_{ab}} \, . \, N_a] \qquad (2)$$

The last square-bracketed term can be written [16] as

$$\frac{1}{2}\frac{\exp(\delta_{ab}/kT) + 1}{\exp(\delta_{ab}/kT) - 1} [(N_b - N_a)T_S - (N_b - N_a)_T]$$

where N_b and N_a are the populations of the eigenstates $|b\rangle$ and $|a\rangle$, T_S is the spin temperature and T the lattice temperature. When $\delta_{ab} \ll kT$ the exponential expansions can be truncated after their second terms and equation 2 becomes

$$w = \frac{3(\delta_{ab})^2 kT}{2\pi\rho v^5\hbar^4} \cdot |\langle a|V_{cf}^{(1)}|b\rangle|^2 \, . \, |(N_b - N_a)_{T_s} - (N_b - N_a)_T| \qquad (3)$$

Hence

$$w \propto (\delta_{ab})^2 \qquad (4)$$

and therefore, for the conditions of the present experiments,

$$T_1 \propto (\delta_{ab})^{-2} \qquad (5)$$

Thus, the influence of the magnetic field is masked until the contribution to δ_{ab} due to the divergence of the energy levels with increasing field becomes dominant. In the present instance the zero-field splitting still constitutes 16% of the total separation of levels 2-3 at 2.6 tesla, the highest field in which measurements were made.

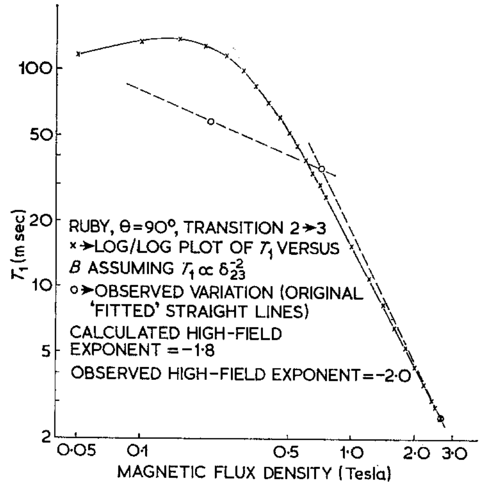

Figure 4 Variation of T_1 with field: ruby, $\theta = 90°$, transition 2-3. [Key:— crosses, log-log plot of T_1 versus B assuming $T_1 \propto \delta_{23}^{-2}$; circles, observed variation (original "fitted" straight lines)]. Calculated high field exponent = −1.8. Observed high field exponent = −2.0.

The effect of the change in δ_{ab} alone is shown in fig. 4. In deriving this the values of δ_{ab} for the fields used in the measurements were obtained from the energy level diagram; the magnitude of T_1 for the highest field, ~ 2.6 tesla, was used as a reference standard and the values for the other fields were found by using equation 5. Over the low field region fig. 4 shows that little variation of T_1 with field will be seen. In the high field region the calculated exponent is −1.8, which agrees closely with the experimentally observed value of −2.0.

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