

Paramagnetic Resonance of the Tripositive Curium Ion in Ethylsulfate and Trichloride Crystals*

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The paramagnetic resonance of the ion Cm^{3+} has been studied by incorporating various amounts of curium in crystals of lanthanum ethylsulfate and anhydrous lanthanum trichloride. For the ethylsulfate crystals, a single line was observed at helium temperatures, characterized by $g_{11}=1.925\pm 0.002$ and $g_{\perp}=7.73\pm 0.02$. A similar line, for which $g_{11}=1.925\pm 0.002$ and $g_{\perp}=7.67\pm 0.02$, occurs for the trichloride crystals. These lines are interpreted as corresponding to transitions within the lowest doublet of the ground level $5f^7\ ^8S_{7/2}$, which, owing to the high degree of intermediate coupling, does not possess the extremely small splitting typical of S states. The Landé g value of the ground level is found to be 1.925. Previous experimental results on the paramagnetic resonance of Cm^{3+} , which were difficult to account for theoretically, are shown to be spurious; evidently the reported spectra should have been ascribed to Gd^{3+} .

A FEW years ago, the paramagnetic resonance spectrum of Cm^{3+} substituted for La^{3+} in the crystal LaCl_3 was reported by a group at Berkeley¹ and, with apparently greater precision, by a group at the Argonne National Laboratory.² Seven lines were observed, characteristic of a level with a total angular momentum, J , of $7/2$, and a Landé g value of 1.991. These results received a ready explanation. The ground state of Cm^{3+} was expected to be $5f^7\ ^8S_{7/2}$, and the spectrum of the rare-earth analog, $\text{Gd}^{3+}\ 4f^7\ ^8S_{7/2}$, had already been found to comprise seven lines for which $g=1.991$.³ From the spread of the seven lines with respect to the external magnetic field, it was concluded that the zero-field splitting of $^8S_{7/2}$ of Cm^{3+} was very similar to that of $^8S_{7/2}$ of Gd^{3+} , though the Argonne group stated that the two spectra were sufficiently dissimilar to be easily distinguished.²

As our knowledge of the actinides has increased, the similarity between the reported spectrum of Cm^{3+} and that of Gd^{3+} has become increasingly embarrassing. The extent of the breakdown of Russell-Saunders coupling should be greater than that for $\text{AmI}\ 5f^7\ ^8S_{7/2}$, for which $g=1.937$.⁴ It should be less than that calculated by Runciman for Cm^{3+} ,⁵ since the recent work of Lämmermann and Conway on PuI indicates that Runciman probably overestimated the spin-orbit coupling constant.⁶ From Runciman's eigenfunctions, we

calculate $g=1.913$, and hence we would expect the g value of the ground level of Cm^{3+} to satisfy the inequality $1.937 > g > 1.913$.

The similarity between the reported zero-field splittings of the ground levels of Gd^{3+} and Cm^{3+} is equally puzzling. Making use of Runciman's eigenfunctions, we find that the ground state of Cm^{3+} comprises only 72% of the pure state $^8S_{7/2}$, and we should expect it to show the minute zero-field splitting characteristic of the ground level of Gd^{3+} only if a highly fortuitous cancellation of the mechanisms that give rise to the splitting occurs.

With these difficulties in mind, experiments were set up to observe (at 9 kMc/sec) the paramagnetic resonance spectrum of Cm^{3+} substituted in small amounts for La^{3+} in lanthanum ethylsulfate and in lanthanum trichloride. In all, five ethylsulfate and two trichloride crystals were grown with varying concentrations of Cm^{3+} . After the experiments, the crystals were assayed to determine the Cm^{3+} concentration, which was found to vary between 1 and 20 μg . For the ethylsulfate crystals, a single line was observed at helium temperatures, characterized by $g_{11}=1.925\pm 0.002$ and $g_{\perp}=7.73\pm 0.02$. A similar line was observed in the trichloride crystals, the parameters being $g_{11}=1.925\pm 0.002$ and $g_{\perp}=7.67\pm 0.02$. No trace was seen of the seven lines previously reported,^{1,2} and it appears quite certain that the spectrum measured earlier was that of Gd^{3+} , not Cm^{3+} . It is remarkable that two groups, working independently, should have made the same erroneous identification.

The observed spectra receive an immediate explanation if the zero-field splitting of the ground level of Cm^{3+} is supposed to be large compared with the energy of the microwave quantum. The single line observed in all crystals corresponds to transitions between the components of the lowest doublet. If this doublet corresponds to $J_z=\pm\frac{1}{2}$, it is easy to show that $g_{11}=g$ and $g_{\perp}=4g$. The value of g_{11} is independent of interactions with higher components of the ground level, and we can immediately conclude that $g=1.925$ for the ground level of Cm^{3+} . This result is consistent with the theory.

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The values of g_1 are very near the theoretical value of $4g$, the slightly lower value for the trichloride possibly being due to the influence of the doublet for which $J_z = \pm \frac{3}{2}$. Such an effect suggests that the splitting of the ground level of Cm^{3+} is smaller in the trichloride than in the ethylsulfate, a result analogous to that for Gd^{3+} in the two crystals.³ This is also suggested by a number of weak, highly anisotropic, lines in the spectrum of the trichloride, some of which may arise from transitions between higher components of the ground level. These are now being investigated.

The present work, by showing the spurious nature of

the earlier observations, eliminates what had become a serious difficulty in the theory; at the same time, it provides an important datum, namely, the Landé g value of the ground level of Cm^{3+} that should be valuable in fixing the degree of intermediate coupling both for Cm^{3+} and, by extrapolation, for later members of the actinide series.

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Weak-Coupling Rate Equations and Initial Conditions*

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Irreversible rate equations for the diagonal and off-diagonal elements of the density matrix are derived in the weak-coupling, long-time approximation for two types of crystal perturbations—electrons scattering from random impurities, and spin-spin interactions. No initial random phase assumption on the density matrix is necessary in the derivation using the random perturbation. For the spin-spin interactions, a “partial” initial random phase assumption is introduced and used in a natural way. It is shown, alternatively, that if one takes into account the very extensive cancellation of terms for the vast majority of unperturbed energy states, no initial restrictions need be placed on the majority of the density matrix elements. In all three cases the equations obtained are the same, being Pauli equations for the diagonal density matrix elements, but simpler relaxation-oscillation equations for the off-diagonal elements.

I. INTRODUCTION

THERE has been considerable interest in the past several years in developing rate equations describing irreversible behavior in many-body systems. The most complete of such equations are the so-called “generalized master equations,” which have been obtained by Prigogine and Résibois,¹ Van Hove,² Janner,³ and Swenson.⁴ The Prigogine-Résibois equations, and the equations obtained earlier by the Prigogine group,¹ apply to gases with interaction, and describe the evolution in time of the diagonal and off-diagonal elements of the density matrix in the quantum-mechanical case. Special initial conditions, but not the random phase assumption, are used. The Van Hove-Janner-Swenson equations apply to any system but describe the time-dependence of the quantities $U_{ij}U^\dagger_{ji}$ (“transition probabilities”) and $U_{ij}U^\dagger_{ki}$ (“interference terms”), where $U(t) = \exp(-iH't/\hbar)$ is the time evolution operator, H' is the total Hamiltonian, and subscript indices denote

matrix elements in an unperturbed energy representation. The initial conditions for the transition probabilities and interference terms are given by the definition of $U(t)$.

The equations mentioned above have the following common property. In spite of the different initial conditions, the density matrix elements, transition probabilities, and interference terms all have Markoffian, irreversible behavior in the weak-coupling, long-time limits.^{2,3,5} Specifically, they all are given by Pauli equations.⁶

The purpose of this paper is to examine the role of initial conditions, and the form of the irreversible rate equations, for two specific but quite different interactions in crystals. We derive rate equations for the density matrix elements in the $\lambda^2 t$ limit (defined below). In each case the Pauli equation obtains for the diagonal density matrix elements but not for the off-diagonal density matrix elements. The first example treats a random perturbation, and it is shown that no initial random phase assumption on the density matrix is necessary. The second example treats spin-spin interactions, and we show that either of two methods may be used to

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