PARAMAGNETIC-RESONANCE STUDY OF THE DYNAMIC JAHN-TELLER EFFECT IN $CaF_2:Sc^{2+}$ AND $SrF_2:Sc^{2+}$†

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(Received 5 December 1966)

Sc^{2+} impurities in CaF_2 and SrF_2 are studied by electron paramagnetic resonance. The Sc^{2+} has an $[Ar]3d^1$ configuration and undergoes a Jahn-Teller distortion. The vibronic states for the equivalent tetragonal distortions couple to give an inversion splitting of roughly 10 cm^{-1}.

This Letter reports the first observation of Sc^{2+} impurity ions by electron paramagnetic resonance (epr) and shows that the electron configuration is $[Ar]3d^1$ for Sc^{2+} substitutional for the cation in CaF_2 and SrF_2. The ScF_8 complex distorts as a result of the Jahn-Teller effect.[1] The types of spectra and the temperature range in which they are observed are explained in terms of the occupation of states of the complex. The states of lowest energy arise from coupling of the vibronic states corresponding to the equivalent distortions of the complex, those of higher energy are rotational-like. Both are a consequency of the dynamic Jahn-Teller effects.

Epr data have been taken on Sc-doped single crystals of CaF_2 and SrF_2 which were x irradiated at room temperature. At 1.5°K and 9.2 GHz with the magnetic field parallel to a ⟨111⟩ axis, a single eight-line hyperfine pattern with a splitting of about 60 G is observed resulting from interaction with the Sc^{45} nucleus ($I=\frac{7}{2}$, abundance = 100%). Each hyperfine line is further split into nine superhyperfine components which have a splitting of 2.2 G and an intensity distribution of about 1:8:28:56:70:56:28:8:1, indicative of an interaction with eight equivalent F^{19} nuclei ($I=\frac{1}{2}$, abundance = 100%) as expected of isolated Sc^{2+} substitutional for Ca^{2+} or Sr^{2+}.

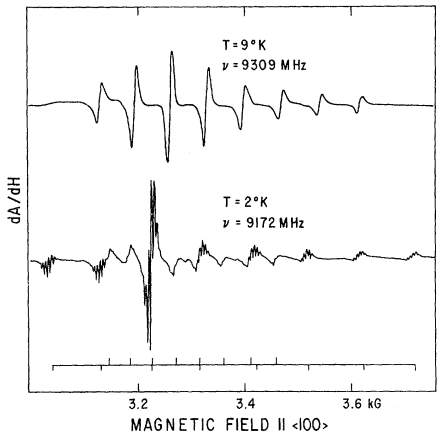

FIG. 1. Epr spectra of $CaF_2:Sc^{2+}$ with $\vec{H}\parallel\langle 100\rangle$. Derivative of absorption versus magnetic field expressed in terms of proton resonance frequency. Above: the isotropic spectrum of the Γ_6 state. Below: the two anisotropic spectra of the Γ_8 state. The positions of the hyperfine lines are indicated by the bar graph at the bottom of the figure.

For arbitrary orientations three different types of spectra are observed in three different temperature ranges. Between 1.5 and 5°K, two anisotropic cubic spectra are observed, as shown in Fig. 1. The angular dependence of the effective g factors is shown in Fig. 2 and has the form

$$g=g_1\pm g_2[1-3(l^2m^2+m^2n^2+n^2l^2)]^{1/2}, \qquad (1)$$

where l, m, and n are the direction cosines of the magnetic field, $\vec{H}$, with respect to the cubic axes of the crystal. The effective hyperfine splitting parameter, K, also fits Eq. (1). The values of g and K for $\vec{H}$ along ⟨100⟩ are given in Table I.

In the temperature range between 5 and about 30°K, an isotropic spectrum is observed (see Fig. 1). Its parameters, also listed in Table I, are an average of the parameters determined

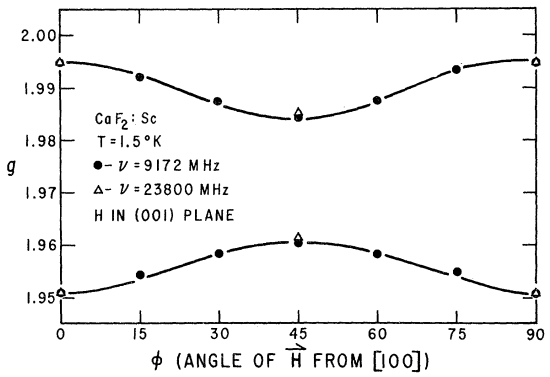

FIG. 2. The g factors of the anisotropic spectra.

Table I. The g factors and hyperfine constants, K, for CaF_2:Sc and SrF_2:Sc, $\vec{H} \| \langle 100 \rangle$.

	CaF_2:Sc		SrF_2:Sc	
	g[a]	K[b]	g[a]	K[b]
Γ_8	1.951	89.5	1.936	91.2
	1.995	40.4	1.991	43.0
Γ_6	1.969	65.5	1.963	67.0
rot.	1.967	65.0	not observed	not observed

[a]The accuray of the g factors is 10^{-3} or better.
[b]Hyperfine constants are given in units of 10^{-4} cm^{-1} with an accuracy of 0.5×10^{-4} cm^{-1}.

for the low-temperature spectrum for $\vec{H}$ along $\langle 100 \rangle$. The intensity, I, of this spectrum satisfies

$$I \propto \{T[2\exp(\Delta/kT)+1]\}^{-1}, \quad (2)$$

where $\Delta \approx 10$ cm^{-1} for CaF_2:Sc and $\Delta \approx 8$ cm^{-1} for SrF_2:Sc. At these temperatures the anisotropic spectra have broadened beyond detection. The anisotropic and isotropic spectra have similar nonuniform amplitude and width distributions. Above 30°K another isotropic spectrum (see Table I) is observed which is described by parameters almost identical to those used for the first isotropic spectrum. However, the amplitude distribution is uniform. This spectrum broadens from 50 to 80°K with the relaxation time, determined through line broadening, proportional to $\exp(\delta/kT)$ ($\delta = 250 \pm 50$ cm^{-1} for CaF_2 and somewhat less for SrF_2).

A Sc^{2+} ion with an $[Ar]3d^1$ configuration has a $^2\Gamma_3$ ground state in the O_h symmetry of the cation site of the CaF_2 lattace. Such an ionic complex is unstable against a tetragonal distortion.[1] The vibronic states for each distortion are coupled because of the low barrier,[2] a process sometimes referred to as tunneling. The weak coupling limit leads to the well-known static Jahn-Teller effect. For coupling comparable with or greater than the anisotropy of the Zeeman terms, such as is the case here, the vibronic states are coupled to give an excited singlet state and a doublet ground state.[3] With spin these become a Γ_6 doublet and a Γ_8 quartet, respectively. The energy parameter Δ in Eq. (2) is called the inversion splitting[4] and is the energy difference between the Γ_8 and Γ_6 states. The temperature dependence of the spectrum up to 30°K results from the occupancy and relaxation of these two states.

For an inversion splitting large compared with the anisotropy of the Zeeman interaction, and the interaction with static strains, the Zeeman effect for the Γ_6 and Γ_8 states can be calculated separately. This together with a small Zeeman anistropy is sufficient to produce an isotropic Γ_6-state epr spectrum and to give an anisotropy to the Γ_8-state epr spectrum of the form shown in Eq. (1). An extension of the treatment of Bersuker[5] and Coffman,[6] who considered the coupling of t_{2g} orbitals into the lower e_g orbitals via the spin-orbit interaction, leads to the expressions $g_1 = 2 + 4\lambda/10Dq$ and $g_2 = 2\lambda(1+\frac{3}{2}\gamma)/10Dq$, where λ is the spin-orbit interaction constant, $10Dq$ is the e_g-to-t_{2g} splitting, and γ is the vibrational overlap. Comparison with our results for CaF_2:Sc gives $\lambda/10Dq = 0.0074$ and $\gamma = 0.24$. Such moderate-coupling theories need modification when extended to large overlap and applied to strain or Zeeman interaction between states of different symmetry.

The uniform isotropic spectrum observed above 30°K results from the occupation of rotational-like excited states. At still higher temperatures this spectrum broadens[7] because of Orbach relaxation to states higher in energy by δ. The large hyperfine anisotropy suggests more complex angular dependence of the Γ_8 hyperfine spectrum than Eq. (1). The observed hyperfine splitting which fits Eq. (1) is not understood and may represent a good test of any proposed theory. The nonuniform width and intensity distributions of the Γ_8 and Γ_6 epr spectra may arise from the coupling of these two states via random internal strains although no consistent description has yet been obtained.

The authors wish to acknowledge the valuable contributions of W. C. Holton and M. de Wit.

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†Work supported in part by U. S. Air Force Office of Scientific Research Contract No. AF49(638)-1250.

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[2]The barrier arises from cubic terms in the Hamiltonian for interaction between electronic and nuclear degrees of freedom [see M. C. M. O'Brien, Proc. Roy. Soc. (London) A281, 323 (1964)].

[3]The symmetric state is higher in energy because of the negative overlap of the electronic functions.

[4]The term inversion splitting is used by analogy with the similar phenomenon in the NH_3 molecule [see, for

example, C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 12]. Similar behavior is also observed for paraelectric and paraelastic defects in crystals [see, for example, P. Sauer, O. Schirmer, and J. Schneider, Phys. Status Solidi 16, 79 (1966)].

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[6]R. E. Coffman, Phys. Letters 19, 475 (1965); 21, 381 (1965). Coffman reports that the part of the Cu^{2+} spectrum in MgO which can be resolved shows the characteristic angular dependence for a Γ_8 state.

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$Ar^{40}(d,p)$ EXCITATION FUNCTIONS OVER THE GROUND-STATE ISOBARIC ANALOG ENERGY REGION*

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(Received 21 December 1966)

In a recent experiment reported by Moore et al.,[1] an anomalous behavior of the excitation function of the reaction $Zr^{90}(d,p)Zr^{91}$ was found. These anomalies occurred at incident deuteron energies corresponding to formation through the (d,n) channel of the $T_>$ states of Nb^{91} whose parent analogs are the ground and first excited states of Zr^{91}. The de-excitation proton yield for the (d,np) reaction was also found to rise sharply in the vicinity of the first anomaly. These anomalies were interpreted as giving evidence for strong coupling between the analog $(Zr+p)$ and $(Nb+n)$ channels.

Following a suggestion by Moore, we have investigated the possibility of a similar effect in the reaction $Ar^{40}(d,p)Ar^{41}$. This target is of interest as the analogs in K^{41} of some of the low-lying states of Ar^{41} are known, from high-resolution measurements at this laboratory,[2] to exhibit fine structure.

According to the Coulomb energy difference of 6.87 ± 0.04 MeV found in Ref. 2, the threshold for excitation of the isobaric analog of the ground state of Ar^{41} through the reaction $Ar^{40}(d,n)K^{41}$ should occur at 2.86 ± 0.04 MeV. We have measured excitation functions from 2.5 to 3.1 MeV for eight of the stronger proton groups shown in Fig. 1 whose l_n values are given in Table I. The data were taken using an on-line DDP-224 computer. The cryogenic gas-target chamber and energy control system for the 3-MeV electrostatic generator have been described elsewhere.[2] Yield curves were taken in steps of 10 keV at a laboratory angle of 135° and with an average beam through the gas target of 30 μA. In order to concentrate initially on the gross-structure effects, we accurately adjusted the energy at each point and then swept the beam energy by ±5 keV. This was accomplished by sweeping the field in the beam-analyzing magnet by the appropriate amount. The curves in Fig. 2 were additionally smoothed by performing a three-point running average. The error bars indicated are computed for the three-point sum and not for the individual count. Because of fluctuations in the effective target density resulting from geometric difficulties, normalization was accomplished by dividing the proton count at each point by the $Ar^{40}(d,$

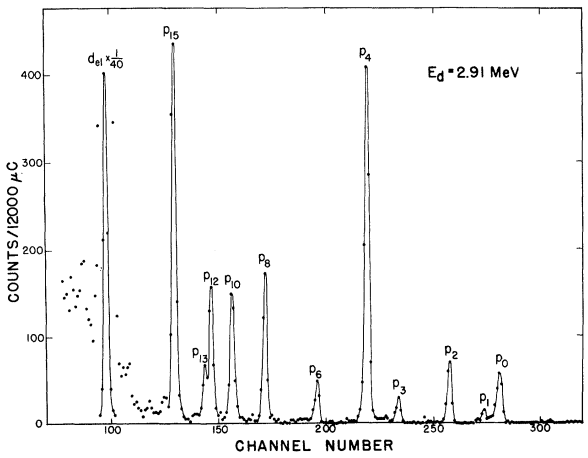

FIG. 1. A typical spectrum for one of the measurements with energy sweep ±5 keV.