STRESS-INDUCED NUCLEAR QUADRUPOLE SPLITTINGS IN MgO:Mn²⁺ AND CaF₂:Eu²⁺

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(Received 22 January 1968)

Stress-induced nuclear quadrupolar splittings are reported for Mn²⁺ and Eu²⁺ in MgO and CaF₂, respectively, using ENDOR techniques. The magnitude of all observed splittings are shown to be in agreement with point-charge estimates, in the absence of any correction for the difference between local and bulk compressibilities. An overlap contribution to the pressure-induced electric field gradient at the nucleus is calculated, and shown to be a factor of 2 smaller than the point-charge contribution. A pressure-induced dipolar contribution, appropriate to CaF₂ stressed along a [111] direction, though calculated to be large (twice the point-charge value), is shown to be absent experimentally.

This Letter reports the first observation of a pressure-induced nuclear quadrupolar splitting for a paramagnetic impurity in a cubic environment. These experiments, using ENDOR techniques, have been performed on divalent Mn⁵⁵ in MgO stressed along the [001] axis, and on divalent Eu¹⁵¹ in CaF₂ stressed along the [001] and [111] axes.

The experiments were carried out at 35 GHz using a standard EPR spectrometer with, however, a provision for the application of a uniaxial stress (up to 1000 kg/cm²) perpendicular to the static magnetic field. The spectrometer used 100-kHz magnetic field modulation, and the modulation loop was also used as the ENDOR radio-frequency loop. All experiments were done with the spectrometer tuned to the electronic transition $S_z = \pm\frac{1}{2} \rightarrow S_z = \mp\frac{1}{2}$, since this transition does not change its position (at these pressures and microwave frequency) with pressure. In order to obtain the greatest accuracy, the EPR lines associated with nuclear projection numbers $I_z = \pm\frac{5}{2}$ were saturated. No observable change of the hyperfine coupling constant A was found, to within experimental error, even at the highest pressure (1000 kg/cm²) used in these experiments.

The results were interpreted using quadrupolar Hamiltonian

$$\mathcal{H} = Q'[I_z{}^2 - I(I+1)], \tag{1}$$

where the axis of stress is taken to be the z direction, and the parameter Q' is defined in terms of microscopic parameters by

$$Q' = 3Qq(1-\gamma_\infty)/4I(2I-1), \tag{2}$$

where Q is the quadrupole moment of the nucleus, q is the pressure-induced electric field gradient at the site of the nucleus, and γ_∞ is the usual Sternheimer antishielding factor.

The experimental values for Q' are listed in Table I, together with the point-charge values calculated using the well-known nuclear quadrupole moments[1,2] $Q(Mn^{55}) = 0.35 \times 10^{-24}$ cm², and $Q(Eu^{151}) = 1.155 \times 10^{-24}$ cm². Values of q were obtained by summing over all points of the distorted lattice. The Sternheimer factors were taken to be[3] $\gamma_\infty = -11.4$ for Mn²⁺, and $\gamma_\infty = -80$ for Eu²⁺. The latter value seems roughly right for divalent ions, since γ_∞ is calculated to lie between −70 and −80 for trivalent rare-earth ions.[3] A glance at Table I shows that remarkable agreement is obtained using this very simple model. No allowance is made for local distortions not equal to bulk distortions. This lack of difference in the bulk and local compressibilities, insofar as the $l = 2$ component of the induced crystalline field is concerned, has been found in previous work on the stress-induced g shifts of rare-earth ions in ThO₂ and CaF₂.[4,5] Part of this insensitivity may arise from the long-range character of the point-charge contributions to the $l = 2$ term in the crystalline potential.

Table I. Experimental and theoretical values of the spin-Hamiltonian coefficient Q' [defined in (1)], per unit stress, for MgO:Mn²⁺ and CaF₂:Eu²⁺. The calculated values are based on a point-charge model, and assume antishielding factors $\gamma_\infty = -11.4$ for Mn²⁺ and $\gamma_\infty = -80$ for Eu²⁺.

	Q' experiment [cps/(kg/cm²)]	Q' calculated [cps/(kg/cm²)]
Mn⁵⁵ in MgO		
Pressure ‖ [001]	+12.5 ± 3	+13.4
Eu¹⁵¹ in CaF₂		
Pressure ‖ [001]	−125 ± 20	−120
Eu¹⁵¹ in CaF₂		
Pressure ‖ [111]	+100 ± 25	+135

There are two other contributions to the electric-field gradient which have been considered in our analysis. The first is that of pressure-induced electric dipoles at the anion sites. These dipoles are absent in MgO for any stress direction, and in CaF_2 for stress along a [001] direction. They are in principle present, however, for stresses along a [111] direction in CaF_2, and have been calculated recently numerically.[4] Assuming an F^- polarizability $\alpha = 0.98$ Å^3, the dipolar polarization alone leads to an electric field gradient twice that of the point-charge contribution, and of the same sign. We argue that such a term is found to be absent experimentally. This follows because, as can be seen from Table I, the calculated point-charge electric field gradient agrees with the experimental value for both [111] and [001] stresses, and the latter induces no electric dipoles by symmetry. Hence, unless the local compressibility is strongly angular dependent, which seems improbable, the quantitative agreement using the point-charge model is significant, and no effect due to stress-induced dipoles appears to be present. This rather strange result is in agreement with other recent measurements referred to above.[4,5]

The second contribution to the electric field gradient arises from differential overlap of the inner occupied p shells and the neighboring ligands.[6] We have analyzed in detail the case of Mn^{2+} in MgO and find[7] the contribution to the electric field gradient of the d electrons to be negligible, and dominant terms to arise from the $3p$ electrons themselves, and the (canceling) off-diagonal contribution of the $2p$ and $3p$ electrons. Possible covalent excitation into the $4p$ shells has been ignored. Using Watson's Hartree-Fock wave functions for the Mn^{2+} and O^{2-} ions,[8] we find an overlap contribution roughly one-half that of the point-charge value, and of the same sign. There are two possible conclusions that may be reached using this result. The first is that, since such good agreement is obtained with a bare point-charge estimate, something must be wrong with the overlap calculation. Indeed, recent calculations have indicated that the O^{2-} Hartree-Fock wave functions are too extended in the MgO lattice,[9] and these conclusions seem to be supported in experiments as well.[10] A second possible interpretation is that the local compressibility is in fact not the same as the bulk compressibility, but is smaller by about 30%. Such a decrease would then, upon adding the overlap and point-charge contributions to the electric field gradient, result in agreement with the experimentally observed values. At the present time we see no way to distinguish between these two alternatives.

*On leave from Czechoslovak Academy of Science, Prague, Czechoslovakia.

†Work supported in part by the National Science Foundation and the U. S. Office of Naval Research, Contract No. Nonr 233(88).

‡Alfred P. Sloan Foundation Fellow.

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