Spin-Lattice Interactions of Ions with Unfilled f-Shells Measured by ESR in Uniaxially Stressed Crystals[†]

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Abstract

The effect of uniaxial stress on the electron-spin-resonance spectra of U^{3+} and Nd^{3+} ions in CaF_2 has been investigated. The uniaxial stress was directed along the [001] and [101] axes, and its effects on the spectra of ions in sites of tetragonal symmetry were observed. Measurements were made at a temperature of 4.2°K and at a frequency of 9.4 GHz. The effect of the applied stress was a shift in the position of a resonance line proportional to the magnitude of the stress. The dependence of this shift on the magnitude and direction of the applied magnetic field was found to be in excellent agreement with that predicted by the inclusion in the spin Hamiltonian of a spin-lattice perturbation of the form, $H_{SL} = \beta h_{ij} S_i H_j$, where h_{ij} is a tensor linearly dependent on the strain in the crystal lattice: $h_{ij} = G_{ijkl} e_{kl}$. In effect, h_{ij} is simply a perturbation added to the normal g-tensor for the ion. For tetragonal symmetry, there are seven independent components of the G-tensor, and these have all been determined for the ions under consideration.

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The spin-lattice interaction for Nd^{3+} and U^{3+} ions at
sites of tetragonal symmetry in CaF_2 has been studied by in-
vestigating the effect of uniaxial stress on the electron-
spin-resonance spectra of these ions. Measurements were
made with stress directed along the [001] and [101] axes,
and were performed at a temperature of 4.2°K and a frequency
of 9.4 GHz. The application of stress resulted in a shift
in the position of each resonance line proportional to the
magnitude of the stress. The observed shifts were found to
be typically 5 to 10 Oe for stresses which resulted in
lattice strain of magnitude approximately 3×10^{-4}.

The strain component along the stress axis was measured
by means of a constantan foil strain gauge bonded directly to
the stressed crystal. The stated gauge factor supplied by
the manufacturer was reduced for operation at 4.2°K by approxi-
mately 10 per cent, in accordance with the measurements of
McClintock (1959). Although the indicated strain was dependent
upon the value of the applied magnetic field, presumably because
of magnetoresistive effects, the incremental strain due to
applied stress was found to be independent of the magnitude
of the field, and a field-independent gauge factor could thus

be used. The estimated accuracy in the measured strain was $\pm 10^{-5}$. The shift in the resonant magnetic field was measured by means of an NMR magnetometer to an estimated accuracy of 0.1 Oe.

The dependence of the observed line shifts on the magnitude and direction of the applied magnetic field was found to be in excellent agreement with that predicted by the inclusion of a perturbation term in the spin Hamiltonian of the form $H_{SL} = \beta h_{ij} S_i H_j$ (summation over repeated indices is implied). In this expression β is the Bohr magneton, S is the effective-spin operator, H is the applied magnetic field, and h_{ij} is a tensor linearly dependent on the lattice strain: $h_{ij} = G_{ijkl} e_{kl}$. In this experiment, the components of the strain tensor could be determined from measurement of the component along the stress axis by using the known elastic constants and the fact that the stress was uniaxial.

This form for H_{SL} is derived essentially in the same manner as that first employed by Van Vleck (1940) to explain spin-lattice relaxation for certain iron-group ions. That is, the stress-induced distortion of the lattice produces a perturbation of the crystalline electric field acting on the ion. To first order, this perturbation to the total electronic Hamiltonian is linear in the strain: $H_I = V_{ij} e_{ij}$. As observed by Orbach (1961), the Kramers-doublet ground state of the ions considered here cannot be split by a perturbation of the

crystalline electric field alone. As a result, the effect
of H_I can be observed only in the presence of a magnetic
field, just as in the case of a naturally occurring crystal-
field component, which would merely lead to a non-iostropic
g-tensor for the ion, in the spin-Hamiltonian formulation.
Thus, the effect of the stress-induced perturbation is simply
a variation of the normal g-tensor. This variation of the
g-tensor is just the h-tensor introduced above. Of course,
a more complicated form for the spin-lattice perturbation to
the spin Hamiltonian would occur if non-linear strain effects
or higher-order perturbation theory were employed. However,
the experimental results reported here are in excellent
agreement with the simple form given above for H_{SL}, and no
more complicated form is considered here.

In order to calculate the effect of applied stress on the
position of a resonance line, it is necessary to determine the
eigenvalues of the total effective-spin Hamiltonina, which,
neglecting hyperfine terms, takes the form $H_s = \beta(g_{ij} + h_{ij})H_i S_j$.
Since the ion has a Kramers-doublet ground state, for which
$S = \frac{1}{2}$, a particularly simple form for the rate of change of
the resonant field with respect to the component of the strain
along the stress axis is found:

$$\partial H/\partial e = (-h\nu/\beta g^3) \, g_{ii} b_i b_j G_{ijkl} (de_{kl}/de).$$

In the above expression, $h\nu = g\beta H_o$ is the unstressed resonance
condition, b_i are the direction cosines of the magnetic field
with respect to the coordinate system in which the g-tensor
is defined, and de_{kl}/de is a tensor whose components are
simple functions of the elastic compliance tensor.

The electronic configurations of the ions U^{3+} and Nd^{3+} are, respectively, $5f^3$ and $4f^3$. In CaF these ions are found primarily in sites of tetragonal symmetry, in which the $^4I_{9/2}$ ground state splits into five Kramers doublets. According to the model proposed by Bleaney, Llewellyn and Jones (1956), the tetragonal symmetry is a consequence of an interstitial charge-compensating F^- ion which may be located along any one of the three principal cube axes, resulting in C_{4v} symmetry at the site of the ion under consideration. Although a small percentage of ions is found in sites of different symmetry, such ions were not considered in the work reported here. The tetragonal symmetry, in a manner similar to that encountered in a consideration of the elastic constants, simplifies the interpretation of the experimental results by greatly reducing the number of independent components of the G-tensor. These components can, therefore, be evaluated with a relatively small number of measurements.

Because of the tetragonal symmetry, the h-tensor is effectively symmetric to an interchange of its indices, and the six-dimensional Voigt notation can be employed wherein each second-rank tensor becomes a column matrix and each fourth-rank tensor becomes a square matrix in six dimensions. Thus, using the same notation for the quantities of interest here, it is possible to write $h_m = G_{mn} e_n$. Again because of the C_{4v} symmetry, many of the components of the G-tensor are zero and many others are equal to each other, and this tensor can be written in Voigt notation in the following way:

$$G_{mn} = \begin{bmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{13} & 0 & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{66} \end{bmatrix}$$

It should be observed that G_{mn} is not symmetric to an interchange of indices, so that G_{13} and G_{31} are not equal. Thus, there are seven independent components of the G-tensor, all of which have been determined by the method reported here for both of the ions under consideration.

In general, each measured line shift was due to a combination of several of the components of the G-tensor, although a few special cases occurred in which the shift was due to a single component. Because of the presence of ions with three different symmetry axes in each experimental sample, however, it was possible to obtain sufficient data for the calculation of all components of the G-tensor with only two samples. In one of these, the stress was applied along the [001] axis, and in the other it was applied along the [101] axis. From measurements on these two samples, it was possible to obtain a least-squares fit of the predicted line shifts to the experimental data, resulting in the following values for the components of the G-tensor for the two ions:

	G_{11}	G_{12}	G_{13}	G_{31}	G_{33}	G_{44}	G_{66}
Nd^{3+}:	4.6 ± 1.0	3.1 ± 1.0	4.6 ± 1.5	1.8 ± 1.0	1.7 ± 1.0	-8.9 ± 0.1	0.1 ± 1.0
U^{3+}:	1.6 ± 0.5	1.3 ± 0.5	1.0 ± 0.5	2.8 ± 1.0	3.2 ± 1.0	-8.9 ± 1.0	-5.9 ± 0.1

The indicated error includes the estimated errors in the measurement of the strain and field values, probable errors in the elastic constants, and other errors which arise from in accuracy of crystal orientation, nonuniformity of stress, etc.

Examples of the comparison of the experimental data with the predicted line shifts using the above values for the G-tensor are shown in Figures 1 and 2. In both cases, the stress axis was in the plane of rotation of the magnetic field, and $\theta = 90°$ corresponds to a situation where the field and stress were parallel. The error bars on the experimental points represent the spread in repeated experimental measurements.

The direct one-phonon spin-lattice relaxation times for these ions have been computed, using the spin-lattice Hamiltonian introduced here, by Donoho and Black (1966). Although some agreement with experimental measurements was found in the case of U^{3+} ions, an enormous disagreement was found in the case of Nd^{3+} ions. This large disagreement is surprising in view of the good agreement between the results of the work reported here and the theory outlined in this paper.

As a verification of this work, an attempt was made by Wetsel and Donoho (1965) to measure the spin-lattice interaction for U^{3+} ions by the method of ultrasonic resonance.

No resonance absorption was observed, however, since the
maximum absorption predicted from the measured G-tensor
was too small to be detected.

References

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Figure Captions

Figure 1: $\partial H/\partial e$ for U^{3+} ions with symmetry about [010],

and with stress applied along [101]. The angular

dependence is simply cos (2θ). Smooth curve rep-

resents least-squares fit.

Figure 2: $\partial H/\partial e$ for Nd^{3+} ions with symmetry about [100],

and with stress applied along [101]. Smooth curve

represents least squares fit.

XERO
COPY

XERO
COPY

U^{3+}

Stress along $[10\bar{1}]$

$[0\bar{1}0]$ – ion

θ (deg)

$\partial H/\partial \varepsilon$ (kOe)

Nd^{3+}
Stress along [101]

[100]-ion

θ (deg)

$\partial H / \partial \epsilon$ (kOe)

Nd Stress along [001]
[100] - ion