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Trace Relations for Tensors Relating Electric Fields and Elastic Strains to Nuclear Quadrupole Effects*

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The effects of electric field and elastic strain on the nuclear quadrupole interactions in crystals have been described by means of third- and fourth-rank tensors relating the change of the electric field gradient tensor components ϕ_{ij} to the components E_k of the applied electric field and to the components e_{lm} of the strain tensor. Usual symmetry relations reduce the number of independent components of the coupling tensors. In addition to the relations due to symmetry, other relations among the components of the coupling tensor have been usually obtained from the assumption that the change in the trace $\Sigma_i\phi_{ii}$ due to applied electric field or strain is equal to zero. We show that the number, but not the interpretation, of the independent tensor coefficients is independent of the assumption about the trace.

THE effect of electric fields in influencing the nuclear quadrupole resonance frequency has been strikingly demonstrated in a series of recent experiments.[1,2] Previously, it had been well known[3,4] that elastic strains could similarly influence the resonance frequency. The description of these effects has been in terms of third- and fourth-rank tensors relating the change of field gradient tensor component ϕ_{ij} with electric field and elastic strain by the equation

$$\delta\phi_{ij}=\sum_k R_{ijk}E_k+\sum_{l,m}S_{ijlm}e_{lm}; \quad (1)$$

e_{lm} is a component of the strain tensor and E_k is a component of the applied electric field, $\phi_{ij}\equiv\partial^2\phi/\partial x_i\partial x_j$ where ϕ is the electrostatic potential at the position of the nucleus being "resonated" and x_i stands for either x,y or z as do the quantities i,j,k,l,m, when used as subscripts in E_k and e_{lm}. The quantities $R_{ijk}\equiv\partial\phi_{ij}/\partial E_k$ are components of a third-rank tensor and the $S_{ijlm}\equiv\partial\phi_{ij}/\partial e_{lm}$ are components of a fourth-rank tensor.

The number of independent components of the **R** tensor and the **S** tensor can usually be drastically reduced by relations which follow from symmetry considerations. The matrix elements of the orientation dependent part of the nuclear quadrupole interaction are independent of the value of $\nabla^2\phi$ at the nucleus. For this reason it is usually stated[1–4] that the number of independent components can be further reduced if one makes use of the relations obtained if the quantities

$$\sum_i R_{iik}=(\partial/\partial E_k)(\sum_i\phi_{ii}) \quad (2)$$

and

$$\sum_i S_{iilm}=(\partial/\partial e_{lm})(\sum_i\phi_{ii}) \quad (3)$$

are assumed equal to zero. Since $\sum_i\phi_{ii}$ is proportional to the electronic charge density at the position of the nucleus being resonated, the "trace relations" fulfilled by setting the right-hand side of Eqs. (2) and (3) equal to zero correspond to a very special assumption about the change of this charge density with the external field or with elastic strains.

The purpose of this note is to point out that the number of independent tensor coefficients to be deduced from experiment is invariant to whether the assumption on the trace is made. However, the interpretation of the numerical values of experimentally deduced coefficients is dependent upon what assumptions are made. That is, the assumption of the trace relations amounts to a hidden change of definition of these coefficients.

The independence of the number of coefficients of the coupling tensors of the value of $\sum_i\phi_{ii}$ follows from the fact that the matrix elements for quadrupole interaction depend only upon the combinations $\phi_{xx}-\phi_{yy}$, $2\phi_{zz}-\phi_{xx}-\phi_{yy}$, ϕ_{xy}, ϕ_{yz}, ϕ_{xz}. For example, consider the three components of the **R** tensor, R_{xxx}, R_{yyx}, R_{zzx}. If we assume $(\partial/\partial E_x)\sum_i\phi_{ii}=0$ then we obtain $R_{xxx}+R_{yyx}+R_{zzx}=0$, reducing by one the number of independent components of **R**. However, even without this assumption, only the two independent combinations, $(R_{xxx}-R_{yyx})$ and $(2R_{zzx}-R_{xxx}-R_{yyx})$ are involved in the orientation-dependent part of the quadrupole interaction. Similarly in the case of the fourth-order tensor, even when relations such as, say, $S_{xxxx}+S_{yyxx}+S_{zzxx}=0$ are not assumed, of the three quantities S_{xxxx}, S_{yyxx} and S_{zzxx} only the two combinations $(S_{xxxx}-S_{yyxx})$ and $(2S_{zzxx}-S_{xxxx}-S_{yyxx})$ enter the quadrupole matrix elements.

The point can be seen most easily for the case of cubic symmetry when all $R_{ijk}=0$ while all $S_{ijlm}=0$ with the exception of $S_{xxxx}=S_{yyyy}=S_{zzzz}$ ($\equiv S_{11}$ in the Voigt notation), $S_{xxyy}=S_{yyzz}=S_{xxzz}\equiv S_{12}$, and $S_{xyxy}=S_{yzyz}=S_{xzxz}\equiv S_{44}$. Only the two quantities $(S_{11}-S_{12})$ and S_{44} are involved in these matrix elements. The trace relation for this symmetry is the vanishing of the quantity $S_{11}+S_{12}$ and would hence fix the relative values of S_{11} and S_{12}.

As mentioned, the assumption of the trace relations is actually equivalent to a redefinition of the quantities R_{ijk} and S_{ijlm}. Thus the field gradient tensor may be

* Some of this work was reported at the 1962 March Meeting of the American Physical Society [Bull. Am. Phys. Soc. 7, 226 (1962)].
[1] T. Kushida and K. Saiki, Phys. Rev. Letters 7, 9 (1961).
[2] J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Letters 7, 11 (1961).
[3] R. B. Shulman, B. J. Wyluda, and P. W. Anderson, Phys. Rev. 107, 953 (1957).
[4] E. F. Taylor and N. Bloembergen, Phys. Rev. 113, 431 (1959).

resolved into a deviatoric tensor

$$\phi_{ij}'=\phi_{ij}-\tfrac{1}{3}(\nabla^2\phi)\delta_{ij} \quad (4)$$

plus its isotropic or scalar part, $\frac{1}{3}(\nabla^2\phi)\delta_{ij}$. The orientation-dependent part of the quadrupole interaction will depend only on the deviatoric part of the field gradient tensor. Equation (1) gives rise to two relations

$$\delta\phi_{ij}'=\sum_k[R_{ijk}-\tfrac{1}{3}\delta_{ij}\sum_n R_{nnk}]E_k +\sum_{lm}[S_{ijlm}-\tfrac{1}{3}\delta_{ij}\sum_s S_{sslm}]e_{lm} \quad (5)$$

and

$$\delta\nabla^2\phi=\sum_k(\sum_n R_{nnk})E_k+\sum_{lm}(\sum_s S_{sslm})e_{lm}. \quad (6)$$

If one defines the tensors R'_{ijk} and S'_{ijlm} by

$$R'_{ijk}=R_{ijk}-\tfrac{1}{3}\delta_{ij}\sum_n R_{nnk} \quad (7)$$

$$S'_{ijlm}=S_{ijlm}-\tfrac{1}{3}\delta_{ij}\sum_s S_{sslm} \quad (8)$$

it is obvious that the assumption of the trace relations previously mentioned amounts to the utilization of Eq. (5) for $\delta\phi_{ij}'$ in terms of the primed quantities:

$$\delta\phi_{ij}'=\sum_k R'_{ijk}E_k+\sum_{lm}S'_{ijlm}e_{lm}. \quad (9)$$

The scalar part of the field gradient tensor whose variation is measured by Eq. (6) cannot be written in terms of the $\mathbf{S}'$ or $\mathbf{R}'$ tensors. It may affect the hyperfine interaction as well as contribute to the isotope shift and nuclear electric monopole transitions. The variation of the scalar part has in fact been measured in certain cases. Benedek and Kushida[5] measured, for example, the variation of Knight shift with hydrostatic pressure. Bloembergen[6] and Pershan[7] observed the variation of the hyperfine structure in MnF_2 with electric field. Equation (6) becomes, in their nomenclature, and where strains are not involved,

$$\delta\nabla^2\phi=\mathbf{F}\cdot\mathbf{E}, \quad (10)$$

where $\mathbf{E}$ is the electric field denoted previously by components E_k. The vector $\mathbf{F}$ reintroduces the three constants which were eliminated by the introduction of the traceless tensor ϕ_{ij}' and the tensor $\mathbf{R}'$. That is, $F_k=\sum_n R_{nnk}$. The combination $\mathbf{R}'$ and $\mathbf{F}$ is equivalent to $\mathbf{R}$.

The number of independent parameters required to describe quadrupole effects is of course independent of whether description is in terms of the primed or unprimed tensors. For example, in the cubic case, the number is equal to two, of which one is $S_{44}=S'_{44}$ and the other is $S_{11}-S_{12}=S'_{11}-S'_{12}$.

The isotropy condition for cubic symmetry for $\mathbf{S}$ is[4] $\frac{1}{2}(S_{11}-S_{12})=S_{44}$. The analog[8] of the Cauchy relations of elasticity theory is $S_{12}=S_{44}$. For the point charge model one can show that $\frac{1}{2}(S_{11}-S_{12})=-\frac{3}{2}S_{12}$. Therefore the Cauchy relation and the isotropy condition are mutually exclusive for the point charge model. The discussion[4] of the apparent violation of the Cauchy relations for NaCl, therefore, is only valid in the context of the point charge model. In general, the compatibility of the Cauchy relation and isotropy requires $S_{11}=3S_{12}$. Since the experiments[3,4] only determine $S_{11}-S_{12}$, the indicated isotropy[4] for NaCl provides no information one way or the other regarding the fulfillment of the compatibility condition.

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[5] G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **5**, 241 (1958).

[6] N. Bloembergen, Phys. Rev. Letters **7**, 90 (1961).

[7] P. S. Pershan and N. Bloembergen, Phys. Rev. Letters **7**, 165 (1961).

[8] The condition for the analog Cauchy relations to hold is that the potential at a nuclear site be expressible in terms of the sum of individual contributions from the other site depending only on the radius vector to these sites. This is obviously true for the point-charge model and would also be true for somewhat more general shielded charge models.