band gives a half-bandwidth of approximately 0.07 eV, $\nu \simeq 10^{18}$ cm^{-3} eV^{-1}, and $N = 1.4\times10^{17}$ cm^{-3}.

We believe that a much more detailed analysis of the band near the Fermi level will be possible with more extensive measurements of the temperature dependence of the dc conductivity.

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†Also at Michelson Laboratory, China Lake, Calif. 93555. Present address: Sandia Laboratories, Albuquerque, N. Mex. 87115.

[1] N. F. Mott, J. Non-Cryst. Solids 8-10, 1 (1972).

[2] V. Ambegoakar, B. I. Halperin, and J. S. Langer, J. Non-Cryst. Solids 8-10, 492 (1972).

[3] M. H. Brodsky, J. Non-Cryst. Solids 8-10, 739 (1972).

[4] H. Fritzsche, in Amorphous and Liquid Semiconductors, edited by J. Tauc (Plenum, New York, to be published).

[5] W. Paul, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972,* edited by the Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972).

[6] N. F. Mott, J. Non-Cryst. Solids 1, 1 (1968).

[7] M. L. Knotek, M. Pollak, T. M. Donovan, and H. Kurtzman, preceding Letter [Phys. Rev. Lett. 30, 853 (1973)].

[8] M. L. Knotek and T. Donovan, Phys. Rev. Lett. 30, 652 (1973).

[9] M. Pollak, J. Non-Cryst. Solids 11, 1 (1972).

[10] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford Univ. Press, Oxford, England, 1971).

[11] We find it worthwhile to point out here that the "apparent" slope (such as one would plot from experimental data in the region of slight curvature in Fig. 2) would deviate slightly from the true $T^{-1/4}$ slope. This would have some effect on the density of states calculated from such an experiment. More importantly, the deviation of the "apparent" slope from the correct slope depends on the width of the localized band. A change in this width from sample to sample could easily cause the crossing of curves reported, for example, in Ref. 3. There are, however, more important reasons why such a crossing may occur. These will be discussed in a separate paper (M. Knotek and T. Donovan, to be published).

[12] T. M. Donovan, W. E. Spicer, and J. Bennett, Phys. Rev. Lett. 22, 1058 (1966); T. M. Donovan, thesis, University of Stanford, 1970 (unpublished).

Anisotropic Exchange Effects in the Exciton Spectrum of $GdCl_3$ and $Gd(OH)_3$

R. L. Cone and R. S. Meltzer
Department of Physics and Astronomy, University of Georgia, Athens, Georgia 30602

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The first detailed application of a general anisotropic exchange operator to energy-transfer problems in magnetic insulators is described for exciton dispersion in $GdCl_3$ and $Gd(OH)_3$. Relationships, which are independent of the two parameters in the theory and are consistent with experiment, are found between transfer-of-energy matrix elements for different excited states, providing strong evidence that anisotropic exchange is the dominant mechanism of energy transfer.

The electronic exchange interaction in insulators is responsible for a variety of phenomena, some of which have not been widely exploited as probes of the *form* of the interaction. In addition to contributing to the magnetic ordering and to the splitting of excited states, it also contributes to energy transfer between ions, to the energy dispersion of excited electronic states, to exciton-magnon interactions, and to multiple-excitation transition mechanisms. The purpose of this paper is to show the importance of the *anisotropic part of the exchange interaction* as a mechanism of energy transfer and dispersion and to illustrate how this can be determined and taken into account in a real system for which there is experimental information.

Anisotropy in the exchange interaction arises from the dependence of the exchange integral on the orbital states of the electrons. Past experiments have shown that this orbital dependence must be taken into account, as the isotropic Heisenberg exchange alone cannot generally explain the phenomena described above.[1-5] Since there are a large number of two-electron exchange integrals (1225 for f electrons and 325 for d electrons[6]), one must carefully choose a system which can be treated with the desired generality regarding the interactions and yet remain amenable to analysis.

In order to reduce the number of parameters in the theory to a tractable number, one can take advantage of the crystalline symmetry and the nature of the electronic states of each magnetic ion. Since the pair symmetry alone is generally *not* a powerful tool for simplifying the interaction, one must rely on the nature of the single-ion states to gain adequate simplifications. Where the exchange interaction has been expanded in terms of two-electron exchange integrals, this has been accomplished by treating systems where only diagonal integrals $[\mathcal{J}(m_a m_b; m_a m_b)]$ appear.[4,5] However, this expansion does not allow one to take advantage readily of the symmetry of the multielectron states. This can best be accomplished by expressing the exchange interaction in terms of tensor operators as described by Levy[6] and Elliott and Thorpe.[7] The parameters which multiply these operators can be directly related to the two-electron exchange integrals [see Eq. (2)]. For simple single-ion states only a small number are required, although a *large* number of two-electron exchange integrals occur.

The present paper illustrates with a simple example that adequate reduction in the number of parameters can be obtained for real systems on the basis of the single-ion states. In particular, it is shown that the dispersion of five exciton states in both $\mathrm{GdCl_3}$ and $\mathrm{Gd(OH)_3}$ can be described with only two anisotropic exchange parameters for each material.

An experimental study of the line shape and position of the magnon → exciton transitions in these materials has enabled Meltzer and Moos[8] to extract the transfer-of-energy matrix elements

$$\langle {}^8S_{7/2}M_J = -\tfrac{7}{2}; {}^6P_J M_J | \mathcal{H} | {}^6P_J M_J; {}^8S_{7/2}M_J = -\tfrac{7}{2}\rangle$$

coupling the ground state ${}^8S_{7/2}M_J = -\frac{7}{2}$ of one Gd^{3+} ion with the excited ${}^6P_J M_J$ states on nearest-neighbor Gd^{3+} ions. The results for nearest neighbors are given in Table I which illustrates that the matrix elements of interest here are comparable with those for the ground state. Although theoretical relationships between two pairs of these matrix elements were found, no theoretical relationship between these and the matrix elements for ${}^6P_{7/2}M_J = -7/2$ could be shown.

TABLE I. Comparison of theory and experiment for matrix elements of the form $\langle g_1 e_2 | \mathcal{H} | e_1 g_2\rangle$ which transfer energy from ion 1 to ion 2 for Gd^{3+} ions in $\mathrm{GdCl_3}$ and $\mathrm{Gd(OH)_3}$. g represents the ground state ${}^8S_{7/2}$, $M_J = -\frac{7}{2}$ and excited states e are given below. Units for the matrix elements are cm^{-1}.

	$\mathrm{GdCl_3}$		$\mathrm{Gd(OH)_3}$	
$\vert SLJM_J\rangle$	Expt[a]	Theory	Expt[a]	Theory
${}^6P_{7/2} - 7/2$	0.21	0.21	0.40	0.39
${}^6P_{7/2} - 3/2$	0.01	0.01	−0.02	0.02
${}^6P_{5/2} - 3/2$	0.08	0.07	0.10	0.12
${}^6P_{7/2} - 5/2$	−0.03	−0.03	0.01	⋯
${}^6P_{5/2} - 5/2$	−0.08	−0.08	⋯	⋯
${}^8S_{7/2} - 5/2$	0.19	⋯	0.44	⋯

[a] See Ref. 8. Errors are ±0.04 and ±0.01 for P and S states, respectively.

We must first determine if interaction mechanisms other than exchange can contribute to the transfer-of-energy matrix elements. These include the magnetic dipole-dipole interaction, the electric multipole-multipole interaction, and virtual-phonon exchange.[2] The free-ion wave functions[9] for Gd^{3+} indicate that the ${}^8S_{7/2}$ and ${}^6P_J$ states are essentially pure with only slight admixtures of ${}^6P$ and ${}^6D$, respectively.[10] If the states were pure ${}^8S$ and ${}^6P$, respectively, *only* the *anisotropic* part of the exchange interaction could give a nonzero contribution to the transfer of energy matrix elements. Matrix elements of the other interactions listed above, *including* the isotropic Heisenberg part of the exchange, would be zero.

When the small admixtures of other states are considered, the magnetic dipole-dipole and isotropic exchange interactions are found to give a negligible contribution to the measured transfer of energy matrix elements. Only the electric quadrupole-quadrupole interaction ($\lesssim 2\ \mathrm{cm}^{-1}$ for rare-earth trihalides[2]) will contribute to the electric multipole interaction. Spin selection rules for electric multipole interactions and the properties of half-filled shells under charge conjugation[11] reduce its contribution by 10^{-3} as they require the *simultaneous* admixture of ${}^6P$ into ${}^8S_{7/2}$ *and* ${}^6D$ into ${}^6P_J$. Thus electric multipole interactions and virtual-phonon exchange, to which similar considerations apply, appear to give negligible contributions to the interaction. We therefore concentrate on the exchange.

The parametrization of the exchange interaction given by Levy[6] is in the form most convenient for problems involving excited levels:

$$\mathcal{H}_{\text{exch}}=\sum_{i,j}^{7,7}\sum_{k,k'}\sum_{q,q'}-\Gamma_{qq'}^{kk'}u_q^{(k)}(i)u_{q'}^{(k')}(j)\{\tfrac{1}{2}+2\vec{s}_i\cdot\vec{s}_j\}. \tag{1}$$

It is given in terms of spherical-tensor operators,[12] which act on the spin and orbital angular momentum of individual electrons, and applies to all states of the $4f^7$ configuration. The $\Gamma_{qq'}^{kk'}$ contain the radial dependence of the exchange integrals and are thus treated as parameters. The $\Gamma_{qq'}^{kk'}$ are related to the two-electron exchange integrals $\mathcal{J}(m_a'm_b';m_am_b)$ by

$$\Gamma_{qq'}^{kk'}=\sum_{m_a',m_a}\sum_{m_b',m_b}(-1)^{m_a'+m_b'}\mathcal{J}(m_a'm_b';m_am_b)\begin{pmatrix} l & k & l \\ -m_a' & q & m_a\end{pmatrix}\begin{pmatrix} l & k' & l \\ -m_b' & q' & m_b\end{pmatrix}. \tag{2}$$

(In particular $\Gamma_{00}^{00}=7J$, where $-2J\vec{S}_1\cdot\vec{S}_2$ is the isotropic Heisenberg exchange.)

Levy has pointed out that types of spin coupling other than those contained in Eq. (1) could arise in the most general case of superexchange,[13] but in the present case no new terms occur, even if the most general operator linear in the single-electron spin and orbital operators is assumed. The relationship between the $M_J=-\frac{7}{2}$ and $M_J=-\frac{3}{2}$ matrix elements which we determine on the basis of Eq. (1), however, breaks down in the general case. The excellent agreement between experiment and the theory relating these two matrix elements can thus be considered strong evidence that Eq. (1) is an adequate parametrization for the present system.

Time-reversal symmetry for the crystal and a Hermitian energy matrix require[3,6]

$$(\Gamma_{qq'}^{kk'})^*=(-1)^{q+q'}\Gamma_{-q-q'}^{kk'},\quad k+k'\text{ even}. \tag{3}$$

If we now make use of the nearest-neighbor pair symmetry (C_{3h}) and the transformation properties of the $u^{(k)}$,[14]

$$\Gamma_{qq'}^{kk'}=(-1)^{q+q'}\Gamma_{q'q}^{k'k};\qquad q+q'=0,\pm3,\pm6,\pm9,\pm12. \tag{4}$$

No further restriction on k and k' arises from these symmetry considerations.

The free-ion wave functions indicate that the largest terms arise from the ${}^8S$ component of the ground state ${}^8S_{7/2}$ and the ${}^6P$ and ${}^6D$ components of the ${}^6P_J$ states.[10] Contributions of other components are down by 10^{-2} and have been ignored. Only terms with $k=k'=1$ can contribute to the matrix elements between ${}^8S_{7/2}$ and the ${}^6P$ components of the ${}^6P_J$ states.[12] Possible values of q and q' are thus $0,\pm1$. Equations (3) and (4) give

$$\Gamma_{1-1}^{11}=\Gamma_{-11}^{11}=(\Gamma_{1-1}^{11})^*;\quad \Gamma_{00}^{11}=(\Gamma_{00}^{11})^*, \tag{5}$$

so two real parameters are involved for the ${}^6P$ states. Similarly, only Γ_{00}^{22} and $\Gamma_{1-1}^{22}=\Gamma_{-11}^{22}$ are involved for the ${}^6D$ components. Contributions of these $k=2$ terms will be reduced by the square of the ratio of the coefficient of the ${}^6D$ admixture into ${}^6P_J$ to that of ${}^6P$ or about $\frac{1}{6}$. Barring the possibility that the $\Gamma_{qq'}^{22}$ are significantly larger than the $\Gamma_{qq'}^{11}$, and considering the experimental accuracy of the matrix elements, it is reasonable to ignore these terms. The agreement of theory and experiment further justifies this assumption.

Matrix elements of the exchange operator of Eq. (1) are evaluated in the Russell-Saunders representation. Since the ground state contains only $M_S=-\frac{7}{2}$, the operator can only couple to the excited-state components with $M_S=-\frac{5}{2}$, so that only $M_L=M_J+\frac{5}{2}$ needs to be considered.[12] Since $M_L=0$ for the ground state, only Γ_{1-1}^{11} will appear in matrix elements for $M_J=-\frac{7}{2}$ or $-\frac{3}{2}$ and only Γ_{00}^{11} for $M_J=-\frac{5}{2}$. The experimental matrix elements correspond to the product of a single Russell-Saunders matrix element, the square of the admixture of ${}^6P$ into ${}^6P_J$, the square of the Clebsch-Gordan coefficient $\langle SM_SLM_L|SLJM_J\rangle$, and the appropriate $\Gamma_{qq'}^{11}$.

The resulting $\Gamma_{qq'}^{11}$ are given in Table II for both $GdCl_3$ and $Gd(OH)_3$. Comparison of theory and experiment is given in Table I. When interpreting the results, it should be kept in mind that the first three matrix elements for each compound depend only on Γ_{1-1}^{11} and that the ratios of these matrix elements are *independent of the*

TABLE II. Nearest-neighbor isotropic and anisotropic exchange parameters for Gd^{3+} ions in $GdCl_3$ and $Gd(OH)_3$. Units for the parameters are cm^{-1}.

Exchange parameter	$GdCl_3$	$Gd(OH)_3$
Γ_{00}^{00}	-0.19 ± 0.01	-0.44 ± 0.01
Γ_{1-1}^{11}	0.28 ± 0.05	0.51 ± 0.05
Γ_{00}^{11}	0.14 ± 0.07	•••

parameter. Likewise, the next two matrix elements for each compound depend only on $\Gamma_{00}{}^{11}$ and the ratio of these is also *independent of the parameter.* The agreement between theory and experiment is thus remarkable.

The agreement for $GdCl_3$ is essentially perfect, with both $\Gamma_{1-1}{}^{11}$ and $\Gamma_{00}{}^{11}$ well determined. For $Gd(OH)_3$ there are insufficient data to determine $\Gamma_{00}{}^{11}$, but $\Gamma_{1-1}{}^{11}$ is well determined. Difference between theory and experiment is greatest for the $J=\frac{7}{2}$, $M_J=-\frac{3}{2}$ state in $Gd(OH)_3$, yet even in this case the calculated matrix element is within experimental error. While this difference could certainly be experimental, it should be noted that the $\Gamma_{1-1}{}^{22}$ term would give its largest contribution to this particular matrix element.

The quality of agreement between theory and experiment provides strong evidence that Eq. (1) is an adequate parametrization of the exchange interaction responsible for the exciton dispersion in the compounds $GdCl_3$ and $Gd(OH)_3$. Moreover, it indicates that the contribution of the *anisotropic terms* in the exchange interaction is by far the dominant mechanism of energy transfer for the ${}^6P_J$ and presumably all excited states of Gd^{3+}. Thus, any realistic analysis of ion-ion interactions involving ions with large orbital admixtures must take into account the anisotropy of the exchange interaction.

The results for $GdCl_3$ and $Gd(OH)_3$ suggest that Eq. (1) can be used in simple cases to establish relationships among transfer-of-energy matrix elements in several excited states. A more interesting possibility arises when it is noted that each nearest-neighbor matrix element for $Gd(OH)_3$ is approximately twice that for $GdCl_3$. This should be considered along with the observations of Cochrane and Wolf,[15] who found that the ground-state Heisenberg exchange integral J for Gd^{3+} nearest neighbors *and* second-nearest neighbors in nine different compounds varied systematically with the metal ion spacing. If indeed the anisotropic exchange parameters $\Gamma_{qq'}{}^{11}$ scale by the same factor as the $\Gamma_{00}{}^{00}$ parameter ($7J$), as the present results indicate, it may be possible in some special cases to deduce the energy transfer in electronically excited states from the crystal structure or the widely known magnetic properties of the ground state.

In extending the work of the present paper, the most obvious case would be to consider other states of Gd^{3+} or other Gd^{3+} or Eu^{2+} compounds. Rare-earth ions other than Gd^{3+} or Eu^{2+} would involve more k values since $L\neq 0$ for the ground state; however, such an analysis might still be possible. We are presently considering the possibility of parametrizing the exchange for several transition metal ions which have orbital singlet ground states.

The anisotropic nature of the transfer-of-energy matrix elements for the ${}^6P_J$ excited states has important implications for the ground state of Gd^{3+} (or Eu^{2+}). Spin-orbit coupling admixes 2% ${}^6P$ into ${}^8S_{7/2}$ for Gd^{3+}; therefore, there must be an anisotropic contribution to the ground-state exchange. Indeed, anisotropic biquadratic terms have been found in the spin Hamiltonian of nearest-neighbor Gd^{3+} pairs in $Eu(OH)_3$ by Cochrane, Wu, and Wolf.[16] Preliminary analysis indicates that these terms arise from the $\Gamma_{qq'}{}^{11}$ exchange terms discussed in this paper.

Finally, we should note that knowledge of the anisotropic terms from the present work will provide a much more rigorous test of superexchange models such as those of Bradbury and Newman[17] and thus possibly lead to a better understanding of the nature of these interactions.

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[1] R. J. Birgeneau, J. Chem. Phys. 50, 4282 (1969).

[2] For reviews, see W. P. Wolf, J. Phys. (Paris), Colloq. 32, C1-26 (1971); J. M. Baker, Rep. Progr. Phys. 34, 109 (1971).

[3] R. L. Cone and W. P. Wolf, in *Magnetism and Magnetic Materials—1972,* AIP Conference Proceedings No. 10, edited by C. D. Graham and J. J. Rhyne (American Institute of Physics, New York, 1973), and to be published.

[4] N. L. Huang, Phys. Rev. B 1, 945 (1970).

[5] R. M. Macfarlane and J. W. Allen, Phys. Rev. B 4, 3054 (1971).

[6] P. M. Levy, Phys. Rev. 177, 509 (1969).

[7] R. J. Elliott and M. F. Thorpe, J. Appl. Phys. 39, 802 (1968).

[8] R. S. Meltzer and H. W. Moos, Phys. Rev. B 6, 264 (1972).

[9] H. M. Crosswhite, private communication. See also B. G. Wybourne, Phys. Rev. 148, 317 (1966).

[10] The square of the ${}^6P$ admixture in ${}^8S_{7/2}$ is 0.02; that of ${}^6D$ in ${}^6P_J$ is 0.13.

[11] Wybourne, Ref. 9.

[12] The orbital operators $u^{(k)}$ are defined by $(l\|u^{(k)}\|l)=(2k+1)^{1/2}$. In particular, $u^{(0)}=(7)^{-1/2}\times$ (identity operator) and $u^{(1)}=(28)^{-1/2}l^{(1)}$ for states with $l=3$, where $l^{(1)}$ is the orbital angular momentum of a single electron in spherical-tensor notation. $\vec{s}$ is the spin of a single electron, and the summation over i and j is over the electrons of each ion.

[13] P. M. Levy, Solid State Commun. 7, 1813 (1969).

[14] The operators $u^{(k)}$ are even under inversion.

[15] R. W. Cochrane and W. P. Wolf, Solid State Commun. 9, 1997 (1971).

[16] R. W. Cochrane, C. Y. Wu, and W. P. Wolf, Bull. Amer. Phys. Soc. 18, 467 (1973).

[17] M. I. Bradbury and D. J. Newman, J. Phys. Chem. Solids 32, 627 (1971).

X-Ray Emission Following Nuclear Reactions

G. Deconninck
Facultês Universitaires, B-5000 Namur, Belgium, and Université de Louvain-la-Neuve,
B-1340 Ottignies, Belgium

and

N. Longequeue
Institut des Sciences Nucléaires, 38-Grenoble, France

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We have recorded and analyzed spectra of x rays following proton and α-particle bombardment of heavy atoms. The normal K x rays are accompanied by satellite peaks originating from nuclear reactions. The phenomenon is very intense in α-induced reactions and it is correlated with (α, xn) cross sections; in the case of proton bombardment the intensity of the phenomenon is surprisingly weak. It is presumed that the ionization is due to internal conversion of residual γ rays.

The emission of x-rays following proton and α-particle bombardment has long been investigated by many experimenters and a detailed study of the phenomenon was reported by Merzbacher and Lewis,[1] who calculated the cross section by using the plane-wave Born approximation. Another method of calculation was examined by Garcia,[2] who used the impulse approximation and took into account the distortion of the particle in the Coulomb field. The cross section for x-ray production is dependent on the fluorescence yield ω_K which converts ionization into x-ray cross sections, and this factor is sufficiently well known in the case of heavy elements. Comparisons of theory and recent experimental data were reported at different incident energies.[3,4] The theory can predict the cross sections with an accuracy estimated at 20%, and the general trend of the variations is well reproduced. The theory can then be used for extrapolation of known cross sections.

In addtion to the normal K x-ray emission, different phenomena have recently been investigated: isotopic-shift effects,[5] projectile z dependence of the K cross sections,[4] and satellite emissions.[6] Until now very little attention has been paid to the influence of nuclear reactions on the x-ray production; indeed, nuclear cross sections are many orders of magnitude lower than atomic cross sections. This is not the case for the so-called (α, xn) nuclear reactions which were discovered in the past few years. For instance, the reaction $^{197}\mathrm{Au}(\alpha, xn)$ has a total cross section of 1.67 b for 40-MeV α particles while the computed cross section for x-ray production is 2.1 b. The effect of nuclear reactions of this type is to increase the atomic number Z of the target; if an atomic x-ray is emitted after the reaction, it will correspond to the element of atomic number $Z+2$. Experimental evidence for this phenomenon was reported in α[7] and ^{14}N bombardment.[8]

In this work we investigate the production of K x-rays following the bombardment of heavy- and medium-weight elements with light projectiles. Targets of natural elements (Pb, Au, W, Hg, Ba, and Sn) were bombarded at different energies with $^{+}\mathrm{H}_2$, $^{+}\mathrm{H}$, and $^{++}\mathrm{He}$ from the isochronous cyclotron at Grenoble. The K x rays were detected at 90° from the beam with a 5-mm-thick Ge(Li) detector ($\Delta E = 0.7$ keV at 0.1 MeV) especially designed for minimizing the Compton background from high energy γ rays. The spectra were recorded with a 4-k analyzer and processed with a PDP 9 computer. Self-supported targets of natural elements (10 mg/cm^2) were used. The average beam current was limited to 0.1 nA and the measurements were made in very short periods of time. No appreciable residual activity was observed under these conditions.

A set of typical spectra is shown in Fig. 1; it corresponds to the bombardment of Pb and Au with protons and α particles. The 49-MeV pro-