Large Quadrupolar Interactions in Rare-Earth Compounds

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Several series of rare-earth compounds have been found to undergo structural phase transitions. For most of them the cause has been the cooperative Jahn-Teller effect. Here we point out that for TmZn and TmCd these transitions are not due to the cooperative Jahn-Teller effect. Rather they are *driven* by quadrupolar pair interactions. In these systems the lattice *follows* the quadrupoles and distorts in such a way as to minimize the Jahn-Teller coupling energy.

The existence of quadrupolar pair interactions in rare-earth metals was recently established.[1] Here we point out that in some intermetallic compounds (1) these interactions are large enough to produce quadrupolar phase transitions and (2) conduction electrons and not the lattice, i.e., the cooperative Jahn-Teller effect (CJTE), are probably the primary mechanism for coupling quadrupoles in such intermetallic compounds.

We will distinguish between phase transitions that can only occur due to deformations of a lattice and those that can take place on a nominally rigid lattice. In the first category, the magnetoelastic interactions (g_θ^2 or B_θ^2/C_θ) dominate and give rise to a phase transition known as the cooperative Jahn-Teller effect. In these transitions the lattice distorts, e.g., from cubic to tetragonal. Some recent examples of CJTE systems are the rare-earth zircons as $DyVO_4$ and $TmVO_4$.[2] These systems can order magnetically at a lower temperature, e.g., $DyVO_4$ undergoes a CJT transition at $T_D = 14$ K and order antiferromagnetically at $T_N = 3.07$ K.

For phase transitions that take place on a nominally rigid lattice we will distinguish between those in which magnetic (time-symmetry breaking) interactions dominate and those for which quadrupolar or other time-even multipolar interactions dominate. Where interactions which break time symmetry are dominant one finds the material undergoes a magnetic phase transitions. The presence of magnetoelastic of Jahn-Teller interactions causes the lattice to distort below the transition temperature; in this limit the distortion is called magnetostriction. Iron is a good example of a system in which the magnetic interactions between ions dominate over the other interactions mentioned above. In a third group are materials in which the time-even multipolar interactions dominate; we will explicitly consider only quadrupolar interactions. These systems undergo a phase transition below which the quadrupoles are ordered, and as was the case for magnetic transitions, the presence of the JT interaction causes the lattice to distort. We call this distortion quadrupolar striction. Solid hydrogen is an example of such compounds but until recently no magnetic materials were found in this category.[3,4] Finally there are systems in which two or all three interactions are comparable in size. For example, in DySb all three interactions are of comparable size.[5,6]

Here we would like to draw attention to TmCd and TmZn as the first examples of *magnetic* materials in which quadrupolar interactions dominate over magnetic and magnetoelastic interactions. In these compounds, the quadrupolar interactions are capable of producing a ferroquadrupolar order even for a clamped or rigid lattice. TmCd was found to undergo a quadrupole-driven phase transition at $T_Q = 3.1$ K and no magnetic ordering has been found until now.[7] Below T_Q the ordered quadrupoles induce a tetragonal strain. TmZn has a quadrupolar transition at $T_Q = 8.55$ K and then at $T_c = 8.12$ K orders ferromagnetically.[3,4] In TmZn a recent neutron diffraction study did not reveal any internal modes while for TmCd there is no evidence either way. All extant data have been nicely fitted on the assumption of a $k = 0$ structural distortion. It is the relative size of quadrupolar pair interactions compared to the magnetic interactions that makes these compounds unique (see Table I).

The size of the magnetoelastic and quadrupolar interactions can be determined by fitting the variation with temperature of the elastic constant that

TABLE I. Comparison of physical properties and energies for TmZn and TmCd [several entries that appeared in Table II of Ref. 4 have been corrected here. In Ref. 4, $B_1^2/(C_{11}-C_{12})_0$, G_1, and K_1 correspond, respectively, to the g_θ^2, $g_\theta^2+I_\theta$, and I_θ used in the text].

	TmZn	TmCd
T_C (K)	8.12	0
T_Q (K)	8.55	3.16
$(\frac{c}{a}-1)\times 10^3$	-9 ± 1	-0.6
W(K)	$+1.21\pm 0.1$	0.95 ± 0.1
x	-0.31 ± 0.02	-0.34 ± 0.03
$\langle O_2^0\rangle$ at $T=1.5$ K	43	26
θ^* (Heisenberg) (K/atom)	8.1	0
G_1 (mK/atom)	25 ± 1	12.5 ± 1
B_1 (K/atom)	-28 ± 3	-12.7 ± 1
$(C_{11}-C_{12})_0$ (10^5 K)	1.51	1.25
$B_1^2/(C_{11}-C_{12})_0$ (mK/atom)	5.5 ± 1	1.3 ± 0.3
K_1 (mK/atom)	19 ± 1	11.2 ± 1
$K_1/[B_1^2/(C_{11}-C_{12})_0]$	4 ± 1	9 ± 3

TABLE II. Ratio of quadrupolar to magnetoelastic coupling for representative rare-earth compounds as determined from the softening of lattice modes. Unless otherwise noted, the mode that softens corresponds to the elastic constant $\frac{1}{2}(C_{11}-C_{12})$.

Compound	I_θ/g_θ^2
Rare-earth zircons	
TbVO$_4$	$-0.30^{a,b}$
DyVO$_4$	-0.001 to -0.25^{c}
TmVO$_4$	-0.28^{d} $-0.40^{a,e}$
TmAsO$_4$	$-0.18^{a,f}$
Rare-earth pnictides	
DySb	-0.36^{g}
Rare-earth zinc	
ErZn	1.3^{h}
TmZn	4^{i}
Rare-earth cadmium	
TmCd	9^{i}

[a] Softening occurs in B_{2g} mode which corresponds to elastic constant C_{66}.

[b] See Ref. 8.

[c] See Ref. 9.

[d] See Ref. 10.

[e] See Refs. 10 and 11.

[f] See Ref. 12.

[g] See Ref. 6.

[h] See Ref. 13.

[i] See Table I.

softens above the transition to the following expression[5]:

$$\frac{C_\theta(T)}{C_\theta}=1-\frac{g_\theta^2\chi_\theta(T)}{1-I_\theta\chi_\theta(T)}=\frac{1-(g_\theta^2+I_\theta)\chi_\theta(T)}{1-I_\theta\chi_\theta(T)} \tag{1}$$

Here g_θ represents the magnetoelastic coupling between a homogeneous strain ϵ_θ and the quadrupolar moment of the $4f$ electrons. The parameter I_θ represents the quadrupolar pair coupling which has contributions from the electric multipole interactions, direct exchange interactions, indirect Coulomb and exchange interactions via conduction electrons, and from the phonons. The single-ion quadrupolar susceptibility $\chi_\theta(T)$, is strongly dependent on the crystal-field scheme appropriate to the compound being studied.

When a system with $g_\theta\neq 0$ undergoes a phase transition which produces a uniform strain ϵ_θ below the transition, the elastic constant C_θ begins to soften above the transition. If the transition is continuous the elastic constant goes to zero at the transition temperature T_D, i.e., the numerator in Eq. (1) is zero so that

$$1=(g_\theta^2+I_\theta)\chi_\theta(T_D). \tag{2}$$

For a discontinuous transition the elastic constant does not go to zero but the transition takes place when the free energies of the phases above and below T_D are equal.

Depending on the relative size of the Jahn-Teller coupling g_θ^2 to the multipolar pair interaction I_θ, we either say that the structural phase transition is driven by the CJTE for $g_\theta^2\gg I_\theta$ or say that for $I_\theta\gg g_\theta^2$ the transition is driven by the multipolar (quadrupolar) pair interactions. For the vast majority of rare-earth systems studied up until now the structural phase transition has been attributed to the CJTE. In Table II we give a representative list of systems and their ratios I_θ/g_θ^2. While the CJTE characterization is appropriate for many of the systems studied we have found it to fail for some of the rare-earth zinc and cadmium compounds studied. In these systems I_θ/g_θ^2 is greater than 1; e.g., TmZn and TmCd are notable exceptions for which this ratio is 4 and 9, respectively.[14] For these systems the transitions are driven by the quadrupolar pair interactions (see Table I); the Jahn-Teller couplings merely cause the lattice to *follow* the quadrupoles. *These systems are the first examples of magnetic compounds in which the quadrupolar pair interactions dominate over the bilinear spin couplings to produce a quadrupolar phase transition before the systems orders magnetically.*[15] It would be a misnomer to call the structural phase transition in TmCd and TmZn a cooperative Jahn-Teller transition because in these systems it is the quadrupolar pair interactions I_θ and not the lattice that drive the transition.

We are able to discuss the contributions from two mechanisms to the quadrupolar coupling I_θ. They are the electric quadrupole-quarupole (EQQ) interaction and the phonon self-energy term. For the cubic rocksalt and cesium chloride structures the $k=0$ optical phonons cannot contribute to I_θ and the only $k=0$ contribution from the phonons comes from the self-energy term[5,16]

$$I_\theta \cong -\frac{1}{N}\sum_{k's}|g_{k's}{}^\theta|^2. \tag{3}$$

This is an *anti*ferroquadrupolar coupling. As it is intrinsically negative, this *may* be the dominant mechanism responsible for the quadrupolar coupling in the rare-earth zircons and pnictides [see Table II ($g_\theta{}^2$ is positive)]. However, for the rare-earth zinc and cadmium compounds the quadrupolar pair coupling is *positive*. Therefore, while the phonon self-energy term Eq. (2) may conceivably contribute to I_θ, it cannot be the dominant mechanism.

We have calculated the direct EQQ-interaction contribution to this quadrupolar coupling parameters K_1 and K_2 (Ref. 17) which we generally labeled as I_θ and find that

$$K_1 = -(e^2/2a)\alpha_2{}^2(\langle r^2\rangle_{4f}/a^2)^2F \tag{4}$$

and

$$K_2 = -2K_1.$$

The lattice sum F is given as

$$F \equiv \tfrac{1}{2}\textstyle\sum_i (4\pi)^{1/2}Y_4{}^0(i)/(R_i/a)^5 \tag{5}$$

and α_2 is the Stevens factor for the quadrupolar moment. This sum converges rapidly and we have calculated the contributions coming from the first three nearest-neighbor shells for the CsCl structure and find

$$\begin{aligned} K_1(\text{TmZn}) &= -2.5 \text{ mK/atom},\\ K_1(\text{TmCd}) &= -2.1 \text{ mK/atom}.\end{aligned} \tag{6}$$

By comparing these contributions to the experimental values found in Table I we note they are of *opposite* sign and much smaller. Screening of the quadrupole moments of the $4f^n$ electrons by outer electrons does not change the sign of the coupling.[18] Therefore the EQQ interaction cannot be the dominant mechanism which gives rise to the quadrupolar couplings K_1 found in TmZn and TmCd.

From the above analysis we can eliminate both the phonon and EQQ contributions to the quadrupolar coupling as the primary source of K_1. We conclude that the dominant mechanism for the quadrupolar pair coupling in the rare-earth intermetallics TmZn and TmCd is the indirect Coulomb and exchange interactions via the conduction electrons, and possibly the direct exchange interaction. The coupling of quadrupoles via conduction electrons is analogous to the Ruderman-Kittel-Kasuya-Yosida interaction which couples spins at different sites through the s-f exchange interaction. For quadrupoles it is the direct and exchange parts of the $4f$–conduction-electron (k-f) Coulomb interaction that contribute to the coupling I_θ.[19] *These are the first systems in which one has been able to identify quadrupolar coupling of an exchange or indirect Coulomb origin which is larger than the bilinear spin coupling.* While some of the details of the k-f interaction are known, not enough is known about the band structure, in particular the nonlocal quadrupolar susceptibility of the conduction electrons, to reliably estimate the contribution of the quadrupolar coupling via the conduction electrons to I_θ.

In summary, TmZn and TmCd are the first two magnetic compounds found in which pair interactions drive a quadrupolar phase transition before the system magnetically orders. The coupling of the quadrupoles to lattice strain and phonon modes are *not* the origin of these interactions. Rather, it is some combination of direct exchange and indirect Coulomb and exchange interactions via conduction electrons or possibly superexchange through intervening anions.

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[14] Compounds may exist for which $I_\theta/g_\theta^2 > 1$ but in which the transition is driven by bilinear spin couplings so that T_c or $T_N = T_D$. HoSb may be in this category. B. Lüthi [in, *Magnetism and Magnetic Materials—1976*, AIP Conference Proceedings No. 34, edited by J. J. Becker and G. H. Lander (American Institute of Physics, New York, 1976)] $I_\theta/g_\theta^2 = 5.5$ and $T_N = T_D$; however, a recent study of HoSb by J. Jensen, N. Hessel Andersen, and O. Vogt (private communication) questions this large a value of I_θ/I_θ^2.

[15] The possibility for a quadrupolar phase transition preceding a dipolar one was proposed by P. M. Levy and H. H. Chen [Phys. Rev. Lett. 27, 1385 (1971)] for the pnictides but they were subsequently found not to exhibit separate transitions.

[16] Removing the linear Jahn-Teller coupling from the Hamiltonian for a cubic system by using the displaced-oscillator technique runs into difficulties when there are noncommuting operators. In these cases, R. J. Elliott [*Proceedings of the International Conference on Light Scattering in Solids, Paris, 1971*, edited by M. Balkanski (Flammarion Press, Paris, 1971), p. 354] and Gehring and Gehring (Ref. 2) have shown that one can approximately remove the coupling by a unitary transformation. The sign of I_θ, Eq. (3), will nonetheless be negative.

[17] See Ref. 4, Eq. (2).

[18] The outer closed shells ($5s^2 5p^6$) normally reduce the quadrupole moment and the coupling while the open-shell electrons, especially the $5d$, increase it. When we consider the outer $5d$,$6s$ electrons itinerant, they mediate an indirect coupling of the quadrupoles (see next paragraph in text). The sign of this indirect coupling can be positive.

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Band-to-Band Luminescence in Amorphous Solids: Implications for the Nature of Electronic Band States

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The observation of band-to-band luminescence from an amorphous solid (a-As_2S_3) shows the existence of localized states at energies considerably above the mobility edge.

The true nature of the electronic states in amorphous solids continues to be a subject of intense investigation. Anderson[1] showed that the electronic states in a disordered system are localized for the case of strong disorder. It was proposed[2,3] that the disorder in amorphous solids is not sufficiently strong so that localization occurs only near the extremities of the band and a sharp transition[3] from localized to extended states occurs at an energy called the mobility edge. Most of the evidence for this picture has come from electronic transport properties. Luminescence from band states would provide direct information about them; however, only sub-bandgap luminescence has been reported.[4-6]

We report in this Letter the first observation of band-to-band luminescence in an amorphous solid. This luminescence process has many novel properties. The luminescence spectrum extends to photon energies much higher than the bandgap energy E_0 deduced from optical absorption measurements. This spectrum shifts to higher energy as the excitation energy $h\nu_{ex}$ is increased and the peak of the spectrum occurs at an energy greater than E_0 for the highest excitation energy. We also observe for the first time anti-Stokes luminescence, i.e., luminescence at energies higher than $h\nu_{ex}$. If this band-to-band luminescence is attributed to recombination of free electrons and holes, we conclude from the data that these free carriers are not thermalized, in contrast to what would be expected for truly extended states. The results are discussed in terms of geminate recombination and Frenkel-type exciton. Knowledge of the nature of the electronic band states (electronic states in the valence and conduction bands) of amorphous semiconductors is essential in understanding many