This energy is obtained only when $\langle O_0^{[2]} \rangle = -2$, and all other moments are equal to zero. Therefore, the system does not have a magnetic moment at $T = 0°K$. At finite temperatures our numerical results confirm that the nonmagnetic state has the lowest free energy when $I_{20} > |I_z|$.

(e) From the phase diagrams we see that biquadratic interactions raise the magnetic-ordering temperature for effective-spin interactions with $\mathcal{S} > 1$. For example, in Fig. 1(b) the magnetic-ordering temperature for a fixed I_z is higher for a finite biquadratic interaction I_{20} (solid curve) than it is when $I_{20} = 0$ (dashed line). This is just the opposite of the spin-1 model where the biquadratic interactions preclude magnetic ordering altogether when the bilinear interactions are small.

The high-temperature behavior of the quadrupoles has not been considered because we have used the molecular field approximation. However, we can rigorously state that there is no macroscopic quadrupole polarization for $T > T_Q$ for all systems with at least cubic symmetry, where T_Q is the quadrupole-ordering temperature, by using symmetry arguments similar to those used by Priest.[7] Even though macroscopic polarization, i.e., long-range order, is not present above the ordering temperature, short-range order does exist. This short-range order is not included in the molecular-field approximation. Regions exist in a solid for $T \gtrsim T_Q$ in which all the quadrupoles are locally aligned; these regions are equally partitioned among the crystallographically equivalent directions. For example, for a system with cubic symmetry, the regions of ordered quadrupoles align themselves equally along the three cubic edges, four body diagonals, or six face diagonals above T_Q. At the quadrupole-ordering temperature one of the easy axes is singled out, and the entire crystal forms a single domain.

In summary, the salient feature of magnetic systems with large biquadratic interactions is the separate quadrupole and dipole phase transitions. For systems with $\mathcal{S} = 1$ the region of the phase diagram for separate transitions to occur is small; it is more probable to find these transitions for models with $\mathcal{S} \geq \frac{3}{2}$, e.g., the rare-earth pnictides which have low-lying states described by effective spins of $\mathcal{S} \geq \frac{5}{2}$.

We would like to thank Mrs. E. S. Oran, Dr. M. Blume, and Dr. M. F. Thorpe for very helpful discussions.

*Work supported in part by the U. S. Air Force Office of Scientific Research, AFSC, under Grant No. AFOSR-70-1909.

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Structural and Magnetic Phase Transitions in the Rare-Earth Pnictides*

Peter M. Levy and H. H. Chen
Department of Physics, New York University, Bronx, New York 10453
(Received 16 August 1971)

The pnictides, a series of rare-earth group-V intermetallic compounds, have the unique property that these cubic materials distort 2–3°K above the Néel point. We are able to explain this unusual behavior by using a model in which the lattice distortions are driven by quadrupole phase transitions which occur at higher temperatures than the magnetic phase transitions.

A recent study of the magnetic susceptibilities and lattice distortions of a series of rare-earth group-V intermetallic compounds, the pnictides, has revealed a unique property. These cubic materials distort 2–3°K *above* the Néel temperature,[1] e.g., DySb has a very abrupt tetragonal distortion ($c/a = 0.993$) at $T^* = 11.5°K$, and orders magnetically at $T_N = 9.5°K$. The differences in

the temperatures at which the lattices distorted and magnetically ordered were noted, but heretofore not properly interpreted. We have interpreted the differences in temperatures as evidence for two separate phase transitions, and we propose an explanation for this unusual behavior.

We are able to explain the unusual behavior of the pnictides by using the results of our study of phase transitions in magnetic systems with large biquadratic interactions, as given in the preceding Letter.[2] By using a model in which the lattice distortions are driven by quadrupole phase transitions, we find that these distortions occur at temperatures T^* greater than the temperatures for magnetic ordering, T_N. With the same model we have been successful in reproducing the first-order nature of the structural transformations, and we find that the ordering of the quadrupoles considerably increases the temperatures at which the systems order magnetically.

In this Letter we will first show that the magnetic $4f$ electrons cause the anisotropic lattice distortions. After relating these distortions to the average quadrupole moments of the magnetic systems, we use the results of Ref. 2 to explain the occurrence of the anisotropic distortions at room temperatures $T^* > T_N$. We specifically consider in this Letter systems with uniform tetragonal lattice distortions, e.g., DySb. However, our theory applies equally to pnictides with trigonal distortions, e.g., TbSb, simply by using the cube diagonal as the quantization axis.

The rare-earth group-V intermetallic compounds have a rock-salt structure, i.e., a simple cubic lattice. In a recent x-ray study of the lattice distortions attendant to the magnetic ordering of the rare-earth pnictides, it was found by Lévy[1] that the temperatures at which the distortions occur are higher than the magnetic-ordering temperatures determined from measurements of the magnetic susceptibilities.[3] Some of the rare-earth pnictides have cubic-to-tetragonal lattice distortions up to 3.5°K above the Néel temperatures of the compounds, e.g., CeSb has $T^* = 19.5$°K and $T_N = 16$°K; other pnictides, such as TbSb, have trigonal distortions, i.e., along a cubic diagonal. For GdSb, where Gd^{3+} is an S-state ion, *no* anisotropic distortion has been observed. Also, as the concentration x of the rare earth is varied in the system $Tb_xY_{1-x}Sb$, the lattice distortions disappear at approximately the same concentration for which this system no longer orders magnetically.[1] The above data are evidence that the cubic-to-tetragonal (trigonal) structural phase transformations are driven by the orbitally degenerate $4f$ electrons of the rare-earth ions.

The relation between uniform equilibrium strains and the thermal expectation values of the electric multipole moments of the $4f$ electrons has been given by Callen and Callen[4]:

$$\bar{\epsilon}_\gamma = (1/C_\gamma) \sum_{l=2,4,6} B_\gamma^{[l]} \langle O_\gamma^{[l]} \rangle . \quad (1)$$

For a tetragonal distortion mode Q_θ of the cubic environment about a rare-earth ion,[5] the strain is given as $\epsilon_\theta = 2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}$, the elastic constant is $C_\theta = \frac{1}{2}(C_{11} - C_{12})$, and the quadrupole operator is given as $O_\theta^{[2]} = O_0^{[2]} = 3J_z^2 - J(J+1)$. The operators $O_\theta^{[4]}$ and $O_\theta^{[6]}$ are fourth- and sixth-degree (rank) polynomials of components of the total angular momentum; they transform according to the same representation θ, under symmetry operations of the cubic point group, as the tetragonal strains ϵ_θ. We have estimated the magnitudes of the magnetoelastic coupling constants $B_\theta^{[l]}$ by using a point-charge model of the orbit-lattice interaction.[1,5] For the rare-earth antimonides, $B_\theta^{[2]}$ is an order of magnitude larger than the fourth- and sixth-rank magnetoelastic constants. Therefore, the tetragonal distortions are proportional to the ordering of the quadrupole; when the quadrupoles order, the lattice will anisotropically distort to accomodate itself to the ordered array of quadrupoles.

For magnetic systems described by bilinear exchange interactions the quadrupoles order at the *same* temperature as the spins. However, as we have shown in Ref. 2, the quadrupoles order before the spins when the biquadratic interactions are greater than the bilinear terms. This is just the situation that occurs in the rare-earth pnictides which display separate phase transitions. These materials are face-centered cubic antiferromagnets with a type-2 ordering.[3,6] The reason biquadratic interactions dominate in these cubic systems is that the nearest-neighbor bilinear exchange interactions cancel one another in the molecular-field approximation.

The Hamiltonian which describes the rare-earth pair interactions and the interactions of the rare earth with the lattice is given in the molecular-field approximation as

$$\mathcal{H} = (B_4O_4 + B_6O_6) - I_{20}\langle O_0^{[2]} \rangle O_0^{[2]} - I_z \langle J_z \rangle J_z . \quad (2)$$

The first term describes the effect of the crystal field,[7] the second term is the biquadratic interaction, and the last term is the bilinear ex-

change interaction. We include the orbit-lattice interaction $V_{OL} = -B_\theta^{[2]}\bar{\epsilon}_\theta O_\theta^{[2]}$ in the Hamiltonian Eq. (2) by replacing the equilibrium strains with the thermal expectation values of the quadrupole moments as given in Eq. (1); this contribution has been absorbed in the Hamiltonian Eq. (2) in the term I_{20}. By using the Hamiltonian Eq. (2) to calculate the thermal averages of the dipole and quadrupole moments of the pnictides, we find that when the biquadratic terms are larger than the bilinear, then the quadrupoles order at a temperature T^* higher than the Néel point T_N. The only effect of the crystal field is to lower the temperatures of the phase transitions, T^* and T_N. As the lattice distortions are driven by the quadrupoles in our model, we now understand why the rare-earth pnictides distort before they magnetically order.

We have considered in detail DySb. The Dy^{3+} ion has a ${}^6H_{15/2}$ ground state; we used crystal-field parameters which produce an overall splitting of the $J=\frac{15}{2}$ ground manifold of 300°K,[8] $B_4 = -8.88\times10^{-3}$°K and $B_6 = 4.27\times10^{-6}$°K. We have simplified our calculation by considering only the ground doublet Γ_6 and the first excited quartet $\Gamma_8^{(1)}$ at 20°K.[9] The bilinear and biquadratic interaction constants are adjusted so that the quadrupoles order at the temperature at which the lattice distorts, T^*, and the dipoles order at the Néel point; we find $I_{20} = 2.36\times10^{-3}$°K and $I_z = 0.217$°K. By using these values of the interaction constants, we find that the quadrupole phase transition is of the first order with a large discontinuity, $\langle O_0^{[2]}\rangle_{T=T^*}/\langle O_0^{[2]}\rangle_{T=0} = \frac{1}{2}$, at T^*; see Fig. 1. The energy of the ordered quadrupole system, $[\frac{1}{2}I_{20}\langle O_0^{[2]}\rangle^2]_{T=0°K} = 11.5$°K, has contributions from the EQQ interaction of ~2°K; from the quadrupole-lattice coupling $(B_\theta^{[2]})^2/C_\theta$ of ~3°K; and there is a major contribution from the indirect quadrupole-quadrupole coupling via the $5d$-like conduction electrons of at least 5°K. We have been able to estimate this latter coupling from our previous work on the paramagnetic Curie temperatures of the rare-earth monophosphides.[10]

A striking feature of our results on DySb is that the spin energy taken alone, $[\frac{1}{2}I_z\langle J_z\rangle^2]_{T=0°K}$, would order the spin for $T \cong 5$°K. The biquadratic terms cause the spin system to order at $T_N = 9.5$°K. Therefore, magnetic-ordering temperatures are appreciably increased by the ordering of the quadrupoles.[11]

In spite of the simplifications introduced we have been able to account for the abrupt lattice distortions which precede the magnetic ordering of DySb (see Fig. 1). To obtain better agreement it is necessary to include the effects of the spin fluctuations on the quadrupole phase transition. As we have used the molecular-field approximation, the bilinear exchange interaction does not have any effect on the quadrupole system above the magnetic-ordering temperature T_N. In addition we should consider contributions from higher-degree pair interactions to the Hamiltonian, Eq. (2), and the effects of the higher-degree magnetoelastic couplings, $l = 4, 6$ [see Eq. (1)], which we have not included in our present study.

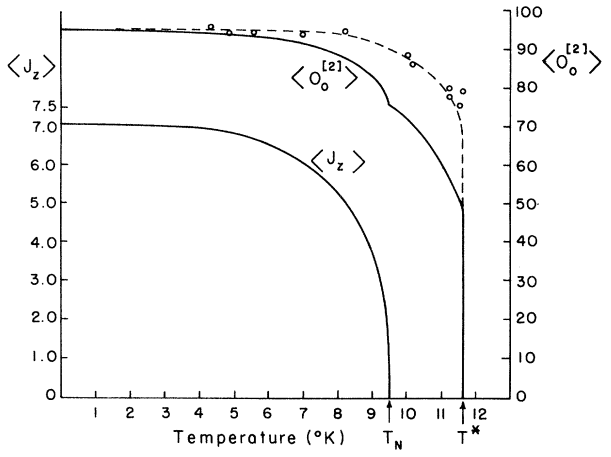

FIG. 1. The solid lines represent the average spin and quadrupole moments of DySb ($J=\frac{15}{2}$) as a function of temperature. The points represent the experimental data on the tetragonal distortions of DySb (Ref. 1). The thermal averages were calculated by using the Hamiltonian Eq. (2) with the parameters $B_4 = -8.88\times10^{-3}$°K, $B_6 = 4.27\times10^{-6}$°K, $I_{20} = 2.36\times10^{-3}$°K, and $I_z = 0.217$°K. When the spins order, the quadrupoles undergo a phase transition of the second order.

In the model presented in this Letter, we considered only parallel arrays of quadrupoles, $I_{20} > 0$; by using the same model with $I_{20} < 0$ we obtain a mutually perpendicular array of quadrupoles.[12] With this revised model we can explain the unusual flopside spin structures found in DyP, DyAs, and HoP.[3,6] As the distortions attendant to this ordering are not uniform, they have escaped detection in previous x-ray studies. However, we predict that careful x-ray and neutron scattering experiments should be able to detect these internal distortions.

In summary, with the model of lattice distortions driven by the ordering of the quadrupoles, we are able to explain the differences in the temperatures T^* and T_N, and to reproduce the first-order nature of the structural phase transforma-

tion. Another consequence of the quadrupole ordering is that it significantly increases the magnetic-ordering temperatures of the pnictides. When we extend this model to DyP, DyAs, and HoP, we can explain the appearance of flopside spin structures.

We should like to thank Professor S. J. Williamson for helpful comments on the manuscript.

*Work supported in part by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR-70-1909.

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Spin Polarization of Photoelectrons from Nickel

Neville V. Smith and Morton M. Traum
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 8 September 1971)

The photoelectron spin polarization in Ni has been estimated numerically using an interpolated band structure and assuming direct optical transitions. In the experimental energy range of Bänninger *et al.*, agreement is obtained for the sign but not the magnitude of the polarization. Detailed predictions for the polarization as a function of both electron energy and photon energy are also presented and display striking variations.

A series of experiments by Bänninger, Busch, Campagna, and Siegmann[1] has revealed that the electron spin polarization (ESP) of photoelectrons emitted from Ni at photon energies just above threshold is positive in sign. A similar result has been obtained on Co and Fe.[2] This is somewhat surprising since the electrons have originated from close to the Fermi level where, on the basis of a Stoner-Wohlfarth-Slater band model, one expects the ESP to be negative (at least for Ni and Co). This interpretation, however, hinges upon the assumption that photoemission experiments sense the density of states (DOS). As noted in a paper by Anderson,[3] the conclusion may be reversed if one takes into account momentum conservation during the optical-excitation event. In such a direct transition approach, photo emission experiments sense not the DOS but rather the energy distribution of the joint density of states[4] (EDJDOS) defined by

$$D(\mathcal{E},\hbar\omega)=(2\pi)^{-3}\sum_{f,i}\int'_{\mathrm{BZ}} d^3k\,\delta(\mathcal{E}_f-\mathcal{E}_i-\hbar\omega)\times\delta(\mathcal{E}_i-\mathcal{E}), \quad (1)$$

where $\mathcal{E}_f$ and $\mathcal{E}_i$ are the electron energies in a final band f and an initial band i, and $\hbar\omega$ is the photon energy. The EDJDOS is essentially the density of states over an optical energy surface in k space, and therefore represents a much more restrictive sampling of the Brillouin zone than the ordinary DOS.

We have performed numerical calculations of the EDJDOS for the majority and minority spin bands of ferromagnetic Ni and have used the results to make various estimates of the photoelectron spin polarization (photo-ESP). We find that, in the photon energy range of Bänninger *et al.*,[1] a positive photo-ESP is predicted. Consequently, a positive sign for the experimental photo-ESP cannot, in itself, be construed as a breakdown of the Stoner-Wohlfarth-Slater band approach. (We hasten to add here that our calculations have been performed only for Ni. Anderson[3] points out that in the case of Ni, even a model based on the DOS could produce fortuitously a positive photo-ESP. Co, with its larger exchange splitting, seems to offer a more serious challenge.) Another per-