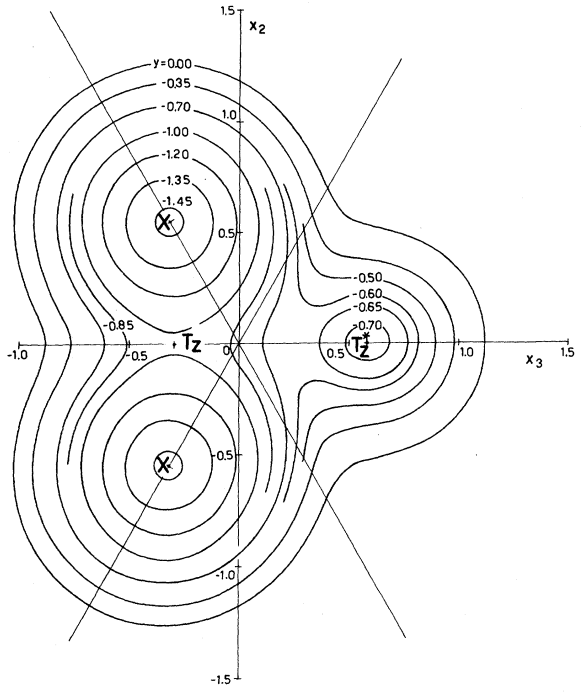

FIG. 4. Same as Fig. 2 for $g = 0.4$ (intermediate coupling). There are two equivalent X minima, the T_z saddle point and a second kind of minimum (T_z*).

suitable values of the parameters A and g, two kinds of minima (T* and X) can coexist on the ${}^3T_{1u}$* APES's.

In conclusion, our analysis shows that Fukuda's interpretation of the experimental features is probably tenable if intermediate coupling is assumed. Nevertheless, a complete understanding of the complex phenomenology of all the phosphors' emission requires the estimation of the parameters A and g for each case. However, this exceeds the purpose of this Letter and will be undertaken in a later, more extensive paper.

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Magnetic and Structural Phase Transition in DySb

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The magnetic properties of DySb have been studied using specific-heat, susceptibility, and neutron scattering techniques. It is found that there is a *single* first-order magnetic phase transition with a marked lattice distortion at 9.5 K. This result is in disagreement with the recent work claiming successive structural (quadrupole) and magnetic phase transitions at 11.5 and 9.5 K, respectively.

In two recent Letters,[1] Levy and Chen have discussed the nature of structural and magnetic phase transitions in systems with appreciable biquadratic as well as bilinear spin-spin interactions, and they have identified the rare-earth pnictides as a class of compounds which exhibit some of the anomalous properties for such systems. In particular, they find that for effective spin $S \geq \frac{3}{2}$ such a system may undergo successive but distinct quadrupole and dipole phase transitions. This theory has been applied by them to DySb as a model example. Based on experimen-

tal work by Levy,[2] they claim that DySb undergoes a quadrupole phase transition with an attendant tetragonal distortion at 11.5 K followed by a magnetic transition at 9.5 K. Stimulated by these predictions, we have carried out a detailed study of the magnetic properties of DySb using specific-heat, susceptibility, and neutron scattering techniques. In this Letter, we report the results of these experiments together with a brief discussion of the properties of DySb in the paramagnetic and ordered regimes.

We consider first the crystal-field theory appropriate to the Dy^{3+} ion. DySb crystallizes in the rock-salt structure with lattice constant $a(20\text{ K}) = 6.143$ Å. At 4.2 K the crystal structure is nearly tetragonal[2] with $a(4.2\text{ K}) = 6.154$ Å, $c(4.2\text{ K}) = 6.113$ Å. The crystal-field Hamiltonian for the Dy^{3+} $^6H_{15/2}$ ground multiplet in the cubic phase may be written

$$\mathcal{H} = A_4{}^0\langle r^4\rangle \chi_4 (O_4{}^0 + 5O_4{}^4) + A_6{}^0\langle r^6\rangle \chi_6 (O_6{}^0 - 21O_6{}^4), \quad (1)$$

where the $O_n{}^m$ are Stevens operator equivalents,[3] and the χ_n are reduced matrix elements. Values for $A_4{}^0\langle r^4\rangle$ and $A_6{}^0\langle r^6\rangle$ may be most reliably obtained by interpolation between spectroscopically measured values in PrSb and TmSb.[4] Using this method we obtain $A_4{}^0\langle r^4\rangle = 86 \pm 6$ K, $A_6{}^0\langle r^6\rangle = 4.2 \pm 1.2$ K. The corresponding crystal-field level scheme for the cubic phase is shown in Fig. 1. The $J = \frac{15}{2}$ manifold is split into two doublets and three quartets with the lowest Γ_6 doublet and $\Gamma_8^{(1)}$ quartet well separated from the higher levels. As a first approximation, one may treat these lowest two levels together as an effective spin $S = \frac{5}{2}$ multiplet.

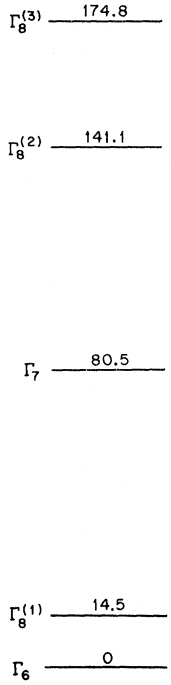

FIG. 1. Crystal-field level diagram for the Dy^{3+} $J = \frac{15}{2}$ ground multiplet in DySb, calculated using the crystal-field parameters given in the text; the energies are in degrees Kelvin.

Consideration of the thermodynamics for the proposed quadrupole and dipolar phase transitions shows there must be an appreciable change in entropy accompanying each one. Thus the existence of these two transitions may be most easily detected via the specific heat. Our experimental results for the specific heat and susceptibility are given in Fig. 2, where the molar specific heat C_m/R is plotted on a logarithmic scale, along with the susceptibility. There is clearly only one single phase transition at $T = 9.518$ K as reported earlier by Busch *et al.*[5] from susceptibility measurements alone, and this transition may be identified as the usual magnetic dipolar ordering. The phase transition is found to be of a relatively sharp first-order nature with a δ function form and a latent heat of 11 ± 2 J/mole. The experimentally observed entropy at 20 K is 14.1 J/K mole which is satisfactorily close to $R \ln 6$

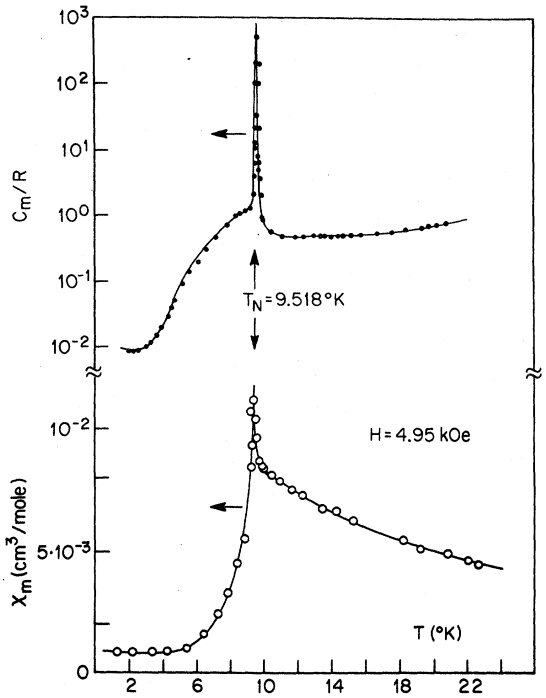

FIG. 2. Specific heat and susceptibility for DySb.

= 14.9 J/K mole. The numerical integration of C/T was stopped arbitrarily at 20 K; the corrections from the lattice and electronic entropy at this temperature, obtained from LuSb and the evaluation of the $1/T^2$ tail from the Γ_8 at 14.5 K, yield approximately opposite corrections of 0.4 J/K mole. An analysis of the nuclear low-temperature specific-heat tail, $\sim 1/T^2$, is in agreement with the elastic neutron scattering data of this work and recent Mössbauer spectroscopy data of Gorobchenko *et al.*[6] that the ordered state carries almost the full saturation moment, close to 10 μ_B.

We now describe briefly the neutron scattering results in DySb relevant to this study.[7] The sample, which was kindly supplied by Gambino, was clamped between two aluminum platelets that apply a pressure along the [001] axis of the crystal. A unique tetragonal axis in the ordered phase was thus successfully obtained, making possible an accurate determination of the positions of the magnetic and nuclear peaks with respect to the tetragonal axis. The results obtained at 5.8 K showed the presence of an antiferromagnetic arrangement of type II, where ferromagnetic sheets are stacked antiferromagnetically along one of the ⟨111⟩ axes. The magnetic moments point along the [001] axis. The positions of the coherent lines are described accurately by a monoclinic chemical cell with a tetragonal contraction of 0.7% with respect to the a axis and an additional 0.1% distortion of the length of the [111] axis coincident with the direction of propagation of the magnetic structure.

The relative occurrence of the magnetic and crystallographic transitions in DySb was checked by monitoring the positions of the nuclear and antiferromagnetic lines as a function of the temperature, as well as the intensity of the magnetic lines. If the antiferromagnetic ordering was to occur at a lower temperature than the crystallographic transition, as suggested by Levy and Chen, then in the intermediate region of temperature the antiferromagnetic lines would be absent and the positions of the nuclear lines would be displaced from the ideal cubic positions. The experimental results are presented in Fig. 3. Here the angle φ between the [111] planes as observed for both magnetic and nuclear reflections is plotted as a function of the temperature. It is apparent that the magnetic and crystallographic transitions for the clamped crystal are smeared out over a region extending from 9.0 to 10.1 K. The clamping is also responsible for a residual tetragonality at 11 K and above. In the transition region, the nuclear peaks gradually shift, while the magnetic peaks drop drastically in intensity but remain at the positions predicted by the distorted lattice. The effect has been interpreted as due to the presence of two phases in the transition region: one essentially cubic and paramagnetic, the other monoclinic (almost tetragonal) and antiferromagnetic. An analysis of the shape of the nuclear peaks in this region shows that they are composed of two components, respectively, in the undistorted and the distorted positions and with relative intensities rapidly changing through the region. The relative volume of the distorted phase accounts completely for the drop of the magnetic intensities between 9 and 10.1 K. Thus it has to be concluded that, from a strictly experimental point of view, the two transitions differ by less than 0.1 K, the limit of reproducibility of the measurements.

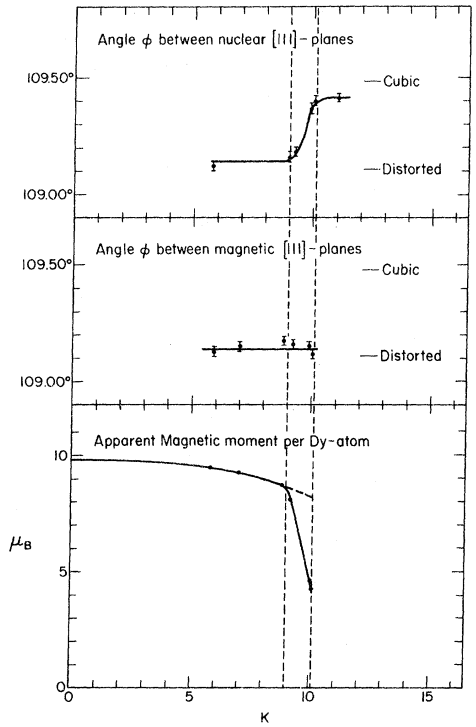

FIG. 3. Neutron scattering results in DySb.

In summary, therefore, DySb exhibits a single first-order magnetic phase transition at 9.5 K. The transition is accompanied by a large (0.7%) tetragonal and somewhat smaller (0.1%) monoclinic [111] distortion; not surprisingly the actual transition temperature is markedly strain dependent. All of these features suggest that DySb does indeed fall into that class of materials characterized by strong biquadratic as well as bilin-

ear interactions, so that to that extent we do confirm Levy and Chen's original hypothesis. However, the ratio of quadrupole-to-dipole terms must be such that there is a single *first-order* transition.[8] Indeed, using the experimental information reported here it should be possible to construct a complete theory for DySb in the molecular field approximation thus yielding explicit values for the quadrupole-quadrupole and dipole-dipole coupling coefficients.

Finally, we should comment briefly on the microscopic origins of the biquadratic terms in DySb. Levy and Chen regard the quadrupole-quadrupole terms as being primarily intrinsic, originating mainly in indirect coupling via the conduction electrons, with the distortions in the ordered phase then following after the fact as a result of the quadrupole-strain coupling. Alternatively, however, the biquadratic interaction could result from virtual-phonon exchange via the quadrupole-lattice coupling so that the transition would then be a cooperative Jahn-Teller and magnetic transition similar to that in UO_2.[9] First-principles or empirical estimates of the various mechanisms are not sufficiently reliable to decide between these two alternatives.[10] Additional experiments on DySb, such as velocity-of-sound measurements, inelastic neutron scattering studies of the elementary excitations, and/or spin-resonance measurements of Dy^{3+} in YSb as a function of strain, should provide the requisite information. We hope that the work reported here will serve to stimulate such additional theoretical and experimental efforts on this most interesting material.

We would like to thank S. J. Allen, Jr., M. Blume, and P. M. Levy for a number of helpful discussions. We should also like to thank P. M. Levy for a critical reading of the manuscript.

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Evidence for Antiferromagnetism in Invar at High Pressures*

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A new phase, most probably antiferromagnetic, is revealed in Invar at high pressures by Mössbauer experiments. In $Fe_{0.70}Ni_{0.30}$ the Néel temperature has a slope of $+1.9\pm0.3$°K/kbar with a zero-pressure intercept of -41 ± 21°K.

There appears to be renewed theoretical interest in the magnetic behavior of concentrated transition-metal alloys as well as the pure metals.[1] Of particular interest is their "localized" versus "itinerant" magnetic character.[2] Invar is interesting in this connection, because, although it appears to be a good example of weak itinerant electron ferromagnetism,[3] we find a localized picture quite appealing in terms of the high-pressure behavior.

Invar is also of interest for its numerous anomalies, which have been the subjects of many recent experiments. In the $Fe_{1-x}Ni_x$ binary alloy system, Invar has $0.29 \leq x \leq 0.45$ with a face-centered cubic structure. Every physical property involving magnetism or volume behaves anomalously in the Invar region compared with the rest of the fcc (γ) range, which extends from In-