Crystal-field effects in PrNi5:
Comparison of calculations with experiments

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In the intermetallic compound PrNi5, exchange interactions between Pr ions are small enough in order not to disturb the crystal-field singlet ground state of the Pr^{3+} ion. The thermodynamic and magnetic properties are thus mainly determined by the crystal-field splitting. It is shown here that magnetic-susceptibility, specific-heat, and thermal-expansion data can be explained satisfactorily with one crystal-field Hamiltonian.

I. INTRODUCTION

Systematic studies of the properties of RCo_5 and RNi_5 intermetallic compounds (R standing for any rare-earth element) date back nearly 20 years, when Wernick et al.[1] first established the hexagonal $CaCu_5$ structure of these materials (see Fig. 4). Magnetic studies by Nesbitt et al.[2] showed that all RCo_5 compounds are ferromagnetic, with a saturation moment larger than that of YCo_5 for R =Sm, Pr, and Nd, and smaller for the heavier rare earth's. This fact was explained by assuming an antiferromagnetic coupling between the ferromagnetically ordered cobalt spins and the s component of the rare-earth local moments, which leads to moment compensation in the case of the heavy rare earth's. All RNi_5 compounds, on the other hand, showed no evidence of ferromagnetic order among the Ni ions. In particular, $YbNi_5$ was still found to be paramagnetic at 1.4 K. Thus in the RNi_5 compounds, the $3d$ shell of the nickel ions seems to be filled by the valence electrons of the rare-earth ions. Except for $PrNi_5$, all RNi_5 compounds are still ferromagnetic at lower temperatures, due to the ordering of the rare-earth moments. The highest ordering temperature of 27 K is found in $GdNi_5$. $PrNi_5$ (in polycrystalline form) is anomalous in that its magnetic susceptibility shows a weak and shallow maximum around 16 K. Early suspicions of an antiferromagnetic transition were discounted by the work of Craig et al.[3] who found that the specific heat shows no anomaly around 16 K, which would be indicative of antiferromagnetic order. These authors then concluded that the susceptibility maximum is a crystal-field effect and that the crystal-field ground state of the Pr ion must be a singlet, leading to Van

Vleck paramagnetism at low temperatures. They were also the first ones who tried to fit a crystal-field Hamiltonian to the specific-heat and susceptibility data. This fit yielded a Γ_4 singlet ground state and first excited states lying 37.9 K (Γ_5 doublet) and 89 K (Γ_3 singlet) above it. It predicted the susceptibility maximum to occur at 20 K for fields applied along the c axis and a smaller susceptibility (with no maximum) for fields normal to the c axis.

Subsequently, we grew the first single crystals of $PrNi_5$ in the course of our work on hyperfine-enhanced nuclear magnetic cooling in Van Vleck paramagnetic Pr compounds.[4,5] The actual susceptibility anisotropy was found to be opposite to the predicted one, which means that the actual crystal-field splitting must be different than that deduced in Ref. 3. Shortly afterwards, more specific-heat as well as thermal-expansion data[6] became available, which further motivated the search for the true crystal-field splitting. A brief summary of the main results of these crystal-field calculations has already been given.[7] In this paper we should like to compare our "best-fit" crystal-field amplitudes with point-charge calculations. Furthermore, we also calculate the crystal-field contribution to the thermal expansion both along and normal to the c axis in the low-temperature range and compare it with observations.

II. CALCULATION OF THE CRYSTAL-FIELD LEVELS

The singlet ground state of the crystal-field-split $^3H_4$ multiplet of Pr^{3+} in $PrNi_5$ remains stable if the exchange interactions between the ions are sufficient-

ly weak. The condition for exchange induced magnetic order is

$$|\lambda| \chi_c > 1 \quad , \tag{1}$$

with

$$\lambda = -\frac{1}{g^2 \mu_B^2} \times 2 \sum_{i<j} J_{ij} \tag{2}$$

being the molecular-field exchange constant, $J_{ij} \vec{J}_i \cdot \vec{J}_j$ the exchange energy between ions i and j which possess total angular momenta $\vec{J}_i$ and $\vec{J}_j$ (in units of h) and χ_c the crystal-field susceptibility. As we shall see below, λ comes out to be 5 mole/emu (positive, ferromagnetic sign). This is about three times smaller than the critical value necessary for induced-moment ordering and means that when taking only nearest-neighbor interactions into account in Eq. (2), the exchange energy between two ions (assuming $J = 4$) is equivalent to -1.6 K. This exchange will lead to a broadening of especially the excited magnetic doublet levels which is of order six (nearest neighbors) times 1.6 K. However, the center of gravity of the individual levels should remain unchanged and still be given by the crystal-field interaction alone. The specific heat and thermal expansion should then remain unaffected to first order by exchange interactions, and their effect on the susceptibility can be taken into account by the usual exchange enhancement formula

$$\chi = \chi_c / (1 - \lambda \chi_c) \quad . \tag{3}$$

At low temperatures, where only the first excited state (at energy Δ above the singlet ground state) is appreciably populated, the specific heat is given by

$$\frac{c}{R} = g_1 \left(\frac{\Delta}{kT}\right)^2 e^{-\Delta/kT} \quad , \tag{4}$$

where g_1 is the multiplicity of the excited state. Analyzing the difference of the specific heat of PrNi$_5$,[6] and that of LaNi$_5$[8] (which is replotted in Fig. 1) between 3 and 8 K yields $\Delta/k = 25.7$ K and $g_1 = 1$. The possible wave functions arising from a $J = 4$ multiplet in a crystal field of hexagonal symmetry are (see, e.g., Ref. 9)

$$\Gamma_1 = |0\rangle \quad ,$$

$$\Gamma_3 = \frac{1}{2^{1/2}}(|+3\rangle + |-3\rangle) \quad ,$$

$$\Gamma_4 = \frac{1}{2^{1/2}}(|+3\rangle - |-3\rangle) \quad ,$$

$$\Gamma_5^1 = a_2|\mp 2\rangle + a_4|\pm 4\rangle \quad \text{(doublet)} \quad , \tag{5}$$

$$\Gamma_5^2 = -a_4|\mp 2\rangle + a_2|\pm 4\rangle \quad \text{(doublet)} \quad ,$$

$$\Gamma_6 = |\pm 1\rangle \quad \text{(doublet)} \quad .$$

The ground state must be either the Γ_3 or Γ_4 singlet. Since we know that the susceptibility along the c axis is smaller than that along the a axis, this first excited singlet state cannot have a matrix element of the operator J_z with the ground state, and therefore must be the Γ_1 state. In order to explain the susceptibility maximum around 16 K in magnetic fields normal to the c axis, it is highly probable that the next higher state is the Γ_6 doublet, since it has a rather strong matrix element of the operator $J_\perp = \frac{1}{2}(J^+ + J^-)$ with the Γ_1 state.

Guided by these requirements, we have searched for suitable solutions of the crystal-field Hamiltonian. Similar to Ref. 3, we write the latter in the form

$$H = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 = W\left\{(1 - |y|)\frac{O_2^0}{F_2} + y\left[x\frac{O_4^0}{F_4} + (1 - |x|)\right.\right.$$

$$\left.\left. \times \left[(1 - |z|)\frac{O_6^0}{F_6} + z\frac{O_6^6}{F_6'}\right]\right]\right\} - g\mu_B \vec{H} \cdot \vec{J} \quad , \tag{6}$$

where the O_n^m are the Steven's equivalent operators and where the four possible crystal-field amplitudes B_n^m can be changed by varying the parameters x, y, and z between -1 to $+1$.

It should be noted that in the work of Ref. 3, the parameter z was not an independent variable since the ratio of the crystal-field amplitudes B_6^0 and B_6^6 was assumed to be constant ($B_6^0/B_6^6 = \frac{8}{77}$). The Hamiltonian in Eq. (6) was diagonalized and the susceptibilities and specific heat were computed from the eigenfunctions using the standard thermodynamic

formula. After about 50 computer runs, we found, by trial and error, a best fit to the susceptibility and specific-heat data for the following set of the parameters:

$$x = 0.18, \quad y = 0.72,$$

$$z = 0.91, \quad W/k = 20.8 K$$

The corresponding eigenfunctions and eigenvalues are tabulated in Table I.
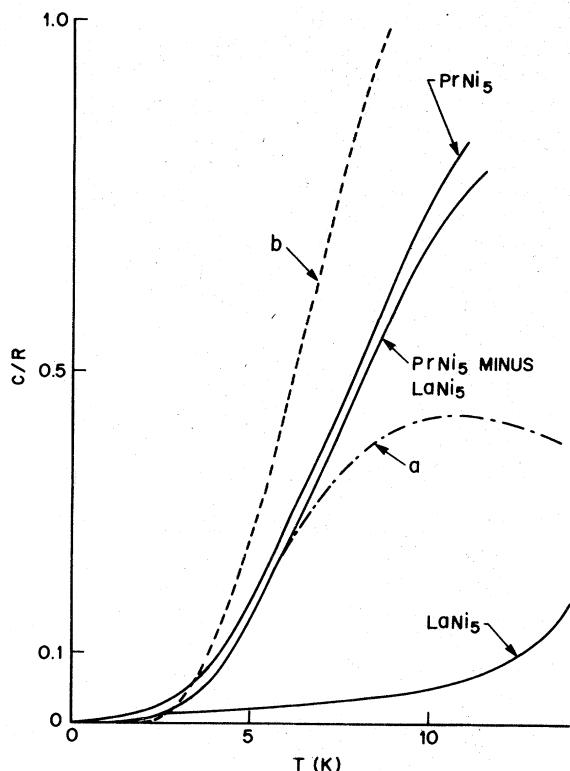
This fit is reproduced in Figs. 2 and 3. The bare

FIG. 1. Low-temperature specific heat of PrNi₅ and LaNi₅ as well as their difference. Also plotted are the theoretical curves for (a) one excited singlet state only at 25.7 K and (b) the overall "best fit" including all levels.
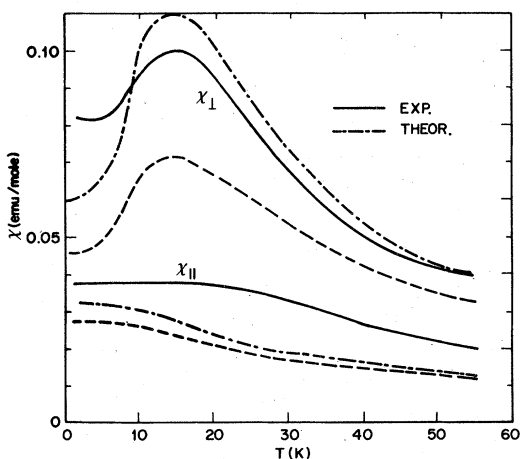
TABLE I. Eigenfunctions and eigenvalues for the "best-fit" parameters $x = 0.18$, $y = 0.72$, $z = 0.91$ and $W/k = 20.8$ K. Also shown are the eigenvalues recently determined by inelastic neutron scattering (Ref. 12).

Eigenfunction		E_i/k (K) (This work)	E_i/k (K) (Ref. 12)
Γ_5'	$0.977\|\pm4\rangle + 0.214\|\mp2\rangle$	332	392.4
Γ_3	$\dfrac{1}{2^{1/2}}(\|+3\rangle + \|-3\rangle)$	156.8	158.6
Γ_5^2	$0.214\|\pm4\rangle - 0.977\|\mp2\rangle$	48.2	54
Γ_6	$\|\pm1\rangle$	39.4	39
Γ_1	$\|0\rangle$	22.9	17.6
Γ_4	$\dfrac{1}{2^{1/2}}(\|+3\rangle - \|-3\rangle)$	0	0

crystal-field susceptibilities come out lower than the observed ones. Using Eq. (3) with a molecular-field constant $\lambda = 5$mole/emu yields the dash-dot lines in Fig. 2. We see that the fit to $\chi_\perp$ is quite reasonable, whereas $\chi_{\parallel}$ comes out somewhat lower than what we observe. (Clearly, a still better fit might be possible by including an anisotropic exchange interaction.) Since the Γ_1 level in the overall fit lies lower (22.9 K) than estimated by Eq. (4) (25.7 K), we overestimate the specific heat at low temperatures, as seen in Figs. 1 and 3. Some of the observed reduction of the peak in the specific heat can be explained by exchange

FIG. 2. Molar magnetic susceptibilities of PrNi₅ for fields parallel and normal to the c axis (solid lines). The dashed lines are the "best-fit" crystal-field susceptibilities, the dash-dot lines their exchange enhanced values.
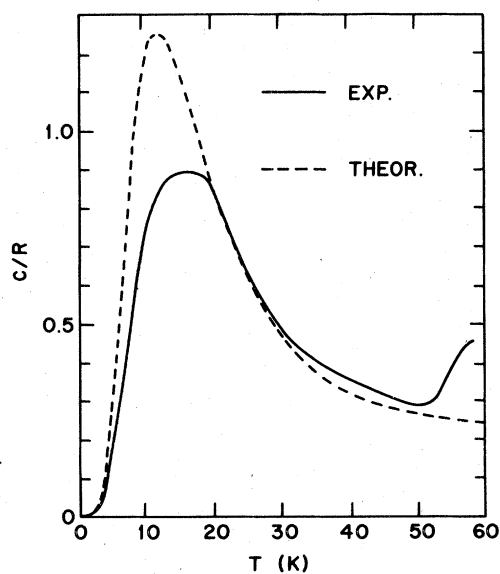

FIG. 3. Specific-heat difference between PrNi₅ and LaNi₅. Above 16 K, the data are those of Ref. 3, below, those of Ref. 6. The dashed line is computed using the "best-fit" crystal-field levels given in Table I.

broadening of the crystal-field levels. At higher temperatures, however, the fit is again quite reasonable. Our systematic search for the "best crystal-field Hamiltonian" has shown that the susceptibility is quite sensitive to changes in the crystal-field amplitudes, and while we do not claim that the solution given in Table I is the best possible one, we believe that a better solution would yield very similar eigenvalues and eigenfunctions.

III. COMPARISON WITH A POINT-CHARGE CALCULATION

It is now of interest to compare the empirically found crystal-field amplitudes B_n^m with those calculated in the point-charge model. Using our "best-fit" parameters given in Table I the empirical values for the B_n^m are

$$B_2^0/k = 5.82 \text{ K}, \quad B_4^0/k = 4.94 \times 10^{-2} \text{ K} ,$$

$$B_6^0/k = 8.77 \times 10^{-4} \text{ K}, \quad B_6^6/k = 3.10 \times 10^{-2} \text{ K} , \tag{7}$$

We now calculate the B_n^m assuming that the crystal field is only due to point charges on nickel ions. Each Pr ion is surrounded by a hexagon of six nearest Ni ions in the same plane and by two hexagons of six next-nearest Ni ions above and below this plane (Figs. 4 and 5). The distance to the nearest Ni ions is $a_0 3^{1/2} = 2.866 \text{ Å}$ and to the next-nearest ions
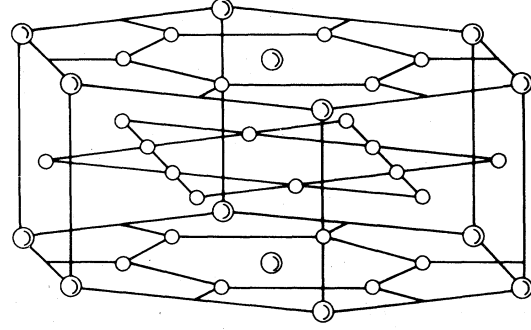
O Ni　　　　　　◎ Pr

CaCu₅ STRUCTURE

FIG. 4. Crystal structure of PrNi₅.

$(a_0/2)R = 3.180 \text{ Å}$, with

$$R = [1 + (c_0/a_0)^2]^{1/2} = 1.281$$

$(a_0 = 4.964 \text{ Å}$ and $c_0 = 3.975 \text{ Å}$ are the lattice parameters of PrNi₅).[10] The calculation of the B_n^m due to these Ni-neighbor ions involves taking sums of tesseral harmonic functions at their location, the origin of the coordinate system being at the Pr ion (for details, see e.g., Ref. 11). We obtain

$$\frac{B_2^0}{k} = -\frac{1}{k} Ze^2 \langle r^2 \rangle \alpha \frac{1}{5} 4\pi \sum_j \frac{Z_{20}(r_j)}{r_j^3} \times \frac{1}{4} \left[\frac{5}{\pi}\right]^{1/2} = +\frac{Ze^2 \langle r^2 \rangle \alpha}{a^3 k} \left[\frac{3 - 6(c/a)^2}{R^5} + \frac{9(3)^{1/2}}{16}\right] = -Z \times 5.087 \text{ K} ,$$

$$\frac{B_4^0}{k} = -\frac{1}{k} Ze^2 \langle r^4 \rangle \beta \frac{1}{9} (4\pi) \sum_j \frac{Z_{40}(r_j)}{r_j^5} \times \frac{3}{16} \left[\frac{1}{\pi}\right]^{1/2}$$

$$= -\frac{Ze^2 \langle r^4 \rangle \beta}{a^5 k} \frac{1}{32} \left[\frac{48(c/a)^4 - 144(c/a)^2 + 18}{R^9} + \frac{3 \times 27 \times 3^{1/2}}{32}\right] = -Z \times 1.341 \times 10^{-3} \text{ K} ,$$

$$\frac{B_6^0}{k} = -\frac{1}{k} Ze^2 \langle r^6 \rangle \gamma \frac{1}{13} (4\pi) \sum_j \frac{Z_{60}(r_j)}{r_j^7} \times \frac{1}{32} \left[\frac{13}{\pi}\right]^{1/2} \quad \tag{8}$$

$$= -\frac{Ze^2 \langle r^6 \rangle \gamma}{a^7 k} \frac{6}{128} \left[\frac{16(c/a)^6 - 120(c/a)^4 - 90(c/a)^2 - 5}{R^{13}} - \frac{5 \times 81}{256(3)^{1/2}}\right] = Z \times 1.733 \times 10^{-5} \text{ K} ,$$

$$\frac{B_6^6}{k} = -Ze^2 \langle r^6 \rangle \gamma \frac{1}{13} (4\pi) \sum \frac{Z_{66}(r_j)}{r_j^7} \times \frac{231}{64} \left[\frac{26}{231\pi}\right]^{1/2} = \frac{Ze^2 \langle r^6 \rangle \gamma}{a^7 k} \frac{231}{128} \left[\frac{1}{R^{13}} - \frac{81}{256(3)^{1/2}}\right]$$

$$= -Z \times 4.683 \times 10^{-4} \text{ K} .$$

NEAREST NEIGHBORS   NEXT NEAREST NEIGHBORS
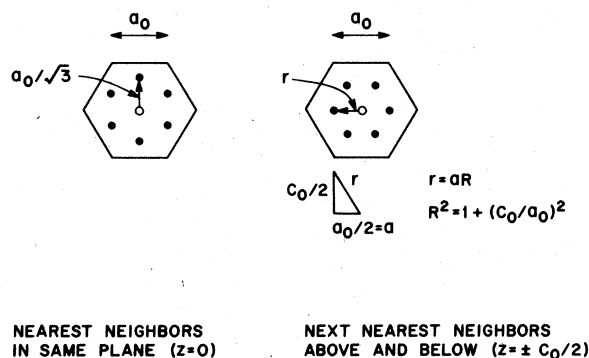IN SAME PLANE (z=0)   ABOVE AND BELOW (z=± c₀/2)

FIG. 5. Location of nearest and next-nearest nickel ions (solid dots) around one Pr ion.

Here Z denotes the ionic charge on the Ni ions in units of $+|e|$ and $a = \frac{1}{2}a_0$. We have used the following values for the Stevens multiplicative factors α_J, β_J, γ_J, and the averages $\langle r^n \rangle$ (Ref. 12) for the $4f$ wave functions:

$$\alpha_J = -0.0210101, \quad \beta_J = -7.34619 \times 10^{-4}$$

$$\gamma_J = 0.60994 \times 10^{-4}, \quad \langle r^2 \rangle = 0.304 \text{ Å}^2$$

$$\langle r^4 \rangle = 0.221 \text{ Å}^4, \quad \langle r^6 \rangle = 0.345 \text{ Å}^6$$

$$e^2/k = 1.67097 \times 10^4 \text{ K Å} ,$$

It should be noted that in contrast to the case of the hexagonal close-packed structure, where the B_2^0 term vanishes for the ideal c/a ratio, the magnitude of the B_2^0 term in Eq. (8) never vanishes and only has a minimum for $c_0/a_0 = 1.22$, as shown in Fig. 6.

Comparing the point-charge values for B_n^m (Eq. 8)
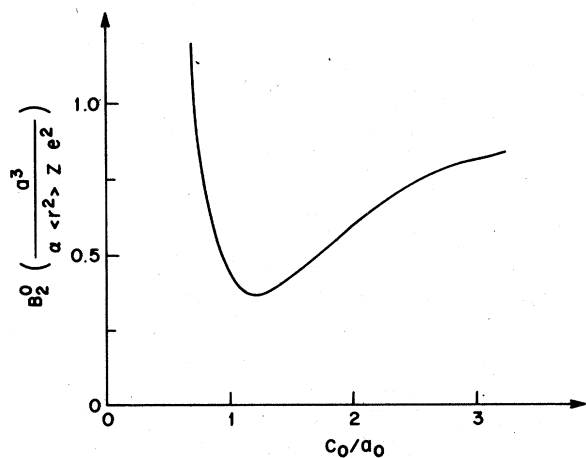

FIG. 6. Variation of the second-order crystal-field amplitude with the c/a ratio in the point-charge model.

TABLE II. Point charges on the nearest and next-nearest nickel ions which would explain the empirically found crystal-field amplitudes.

Amplitude	Point charge (in units of $|e|$)
B_2^0	−1.14
B_4^0	−36.8
B_6^0	+50.6
B_6^6	−66.2

with the empirical ones [Eq. (7)], we see that the second-order term is consistent with a negative charge of about $-|e|$ on the Ni ions, but that all higher-order amplitudes would correspond to considerably larger point charges, as shown in Table II. This breakdown of the point-charge model for the higher-order crystal-field terms is commonly observed in rare-earth compounds, and is most probably due to the fact that a substantial contribution to the crystalline electric field comes from a redistribution of charge of the $5d$ valence electrons of the Pr ion itself, a contribution which we have completely neglected here. Nevertheless, we can conclude from the B_2^0 term that the Ni ions are negatively charged. This is consistent with the idea that the nickel $3d$ states are filled and the nickel ions are nonmagnetic.

IV. CALCULATION OF THE CRYSTAL-FIELD CONTRIBUTION TO THE THERMAL EXPANSION

A large and very anisotropic thermal expansion has been observed in single crystals of PrNi₅,[6] which was as yet unexplained. The observed expansion coefficient is reproduced in Fig. 7. It is negative along the c axis and positive normal to it. Because of its large magnitude, it must be mostly due to crystal-field effects. The only other noteable contribution (at least below ~8 K) is a linear electronic term, which happens to have the same type of anisotropy. Since we now know the crystal-field level scheme, we have attempted to explicitly calculate the crystal-field contribution to the thermal expansion.

According to thermodynamics, the thermal expansion along the axis i of a crystal is determined by the sensitivity of the temperature derivative of the free energy to stress in the direction i (Maxwell's relations)

$$\frac{\partial \epsilon_i}{\partial T} = -\frac{1}{V} \frac{\partial^2 F}{\partial T \partial \sigma_i} . \qquad (9)$$

The relation between stress σ and strain ϵ in a crystal

is (in Voigt's notation)

$$\epsilon_i = s_{ik}\sigma_k, \quad i,k = 1,2,3 \quad , \tag{10}$$

where the s_{ik} are the compliance factors. Using Eq. (10), the right-hand side of Eq. (9) can be transformed in the usual way into a sum of *strain* derivatives of $\partial F/\partial T$. In the case of PrNi$_5$ it is more convenient to work with the variables a and c/a instead of the ϵ_i. Their relation is

$$\frac{\delta a}{a} = \frac{1}{2}(\epsilon_1 + \epsilon_2), \quad \frac{\delta c}{c} = \epsilon_3 \quad . \tag{11}$$

We now rewrite Eq. (9) in terms of derivatives with respect to a and c/a

$$\frac{\partial \epsilon_i}{\partial T} = -\frac{1}{V}\frac{\partial^2 F}{\partial T \partial a}\frac{\partial a}{\partial \sigma_i} - \frac{1}{V}\frac{\partial^2 F}{\partial T \partial (c/a)}\frac{\partial (c/a)}{\partial \sigma_i} \quad . \tag{12}$$

Making again use of Eqs. (10) and (11) we finally obtain the following expressions for the thermal expansion coefficient in the two principal directions:

$$\frac{1}{c}\frac{\partial c}{\partial T} = -\frac{a}{4V}\frac{\partial^2 F}{\partial T \partial a}(2s_{13} + 2s_{23}) - \frac{c/a}{2V}\frac{\partial^2 F}{\partial T \partial (c/a)}(2s_{33} - s_{13} - s_{23}) \quad ,$$

$$\frac{1}{a}\frac{\partial a}{\partial T} = -\frac{a}{4V}\frac{\partial^2 F}{\partial T \partial a}(s_{11} + s_{22} + s_{21} + s_{12}) - \frac{c/a}{2V}\frac{\partial^2 F}{\partial T \partial (c/a)}[s_{31} + s_{32} - \tfrac{1}{2}(s_{11} + s_{22}) - \tfrac{1}{2}(s_{21} + s_{12})] \quad . \tag{13}$$

Unfortunately, we have so far no knowledge of the compliance moduli s_{ik} for PrNi$_5$. Comparing with other hexagonal metals, however, we can at least predict the signs of the s_{ik} sums in Eq. (13). Making use of the symmetry relations $s_{11} = s_{22}$ and $s_{13} = s_{23}$, we obtain

$$s_c^- = 2s_{13} + 2s_{23} = 4s_{13} = \text{negative} \quad ,$$

$$s_c^+ = 2s_{33} - s_{13} - s_{23}$$

$$= 2(s_{33} - s_{13}) = \text{positive} \quad ,$$

$$s_a^- = s_{31} + s_{32} - \tfrac{1}{2}(s_{11} + s_{22}) - \tfrac{1}{2}(s_{21} + s_{12})$$

$$= 2s_{13} - (s_{11} + s_{12}) = \text{negative} \quad ,$$

$$s_a^+ = s_{11} + s_{22} + s_{21} + s_{12}$$

$$= 2(s_{11} + s_{12}) = \text{positive} \quad .$$

With the further abbreviations

$$y_a = -\frac{a}{4V}\frac{\partial^2 F}{\partial T \partial a}$$

and

$$y_{c/a} = -\frac{c/a}{2V}\frac{\partial^2 F}{\partial T \partial (c/a)} \quad , \tag{14}$$

we can finally write Eq. (13) in the form

$$\frac{1}{c}\frac{\partial c}{\partial T} = y_a s_c^- + y_{c/a} s_c^+ \quad ,$$

$$\frac{1}{a}\frac{\partial a}{\partial T} = y_a s_a^+ + y_{c/a} s_a^- \quad . \tag{15}$$

The quantities y_a and $y_{c/a}$ are determined by the sensitivity of the crystal-field levels to changes in the lattice parameter a (at constant c/a) and to changes in ratio c/a (at constant a). We now assume that the relative changes of all crystal-field amplitudes upon changes in a and c/a is the same as that for the point-charge amplitudes. This can really be expected

to be true only for the second-order term (see Table II), since only this term seems to agree in magnitude with a point-charge calculation. To obtain the changes in the energies E_i upon changes δa and $\delta(c/a)$ we first compute (in the point-charge model) the relative changes ΔB_n^m caused by the changes Δa and $\Delta(c/a)$. We then determine the shifted eigenvalues with our computer program in order to be able
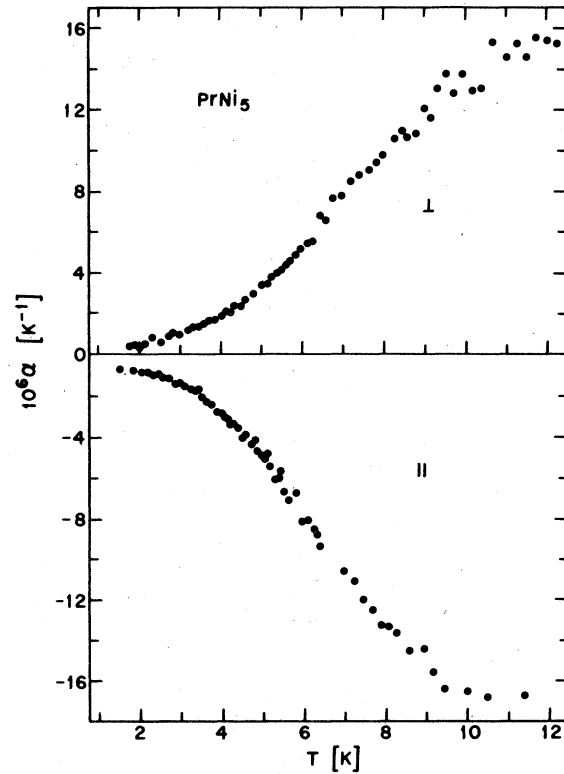

FIG. 7. Thermal expansion coefficients of PrNi$_5$ along and normal to the hexagonal c axis at low temperatures.

to calculate the free energy derivatives

$$\frac{\partial^2 F}{\partial T \partial u} = -\frac{1}{kT^2} \frac{\sum E_i e^{-\beta E_i} \times \sum \left[\frac{\Delta E_j}{\Delta u}\right] e^{-\beta E_j}}{Z^2}$$

$$+\frac{1}{kT^2} \frac{\sum E_i \left[\frac{\Delta E_i}{\Delta u}\right] e^{-\beta E_i}}{Z} \quad , \tag{16}$$

(Z is the partition sum) which is needed to determine y_a and $y_{c/a}$ in Eq. (14). In Eq. (16), Δu stands for Δa and $\Delta(c/a)$.

To get a feeling of the contribution of the individual crystal-field amplitudes to the thermal expansion, we have calculated the quantity y_a under the constraint that only one of the four crystal-field amplitudes is strain dependent. These four computer plots are shown in Fig. 8. Similar curves are obtained for $y_{c/a}$, except that those where B_6^0, respectively, B_6^6 only are varied are of opposite sign. It can be seen that all curves show maxima in the same temperature range where the thermal expansion data (Fig. 7) are suggestive of a maximum (around 12 K). For arbitrary elastic constants, the calculated y_a and $y_{c/a}$ curves have the proper sign to yield a negative expansion along the c axis and a positive one along the a axis, except for two cases: When considering the B_2^0 term only, it yields the wrong sign (negative) for y_a, and when considering the B_4^0 term only, it yields the wrong sign (positive) for $y_{c/a}$. In Eq. (15), the dominant elastic constant is usually s_c^+. Thus for
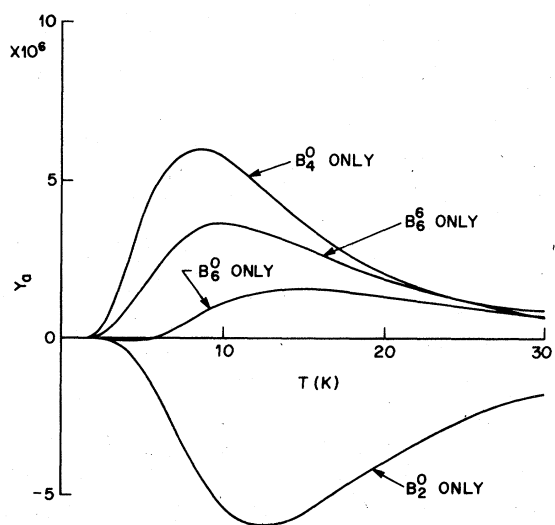
FIG. 8. Plot of parameter y_a vs temperature, when considering only the strain dependence of individual crystal-field amplitudes B_n^m as indicated (see also text).
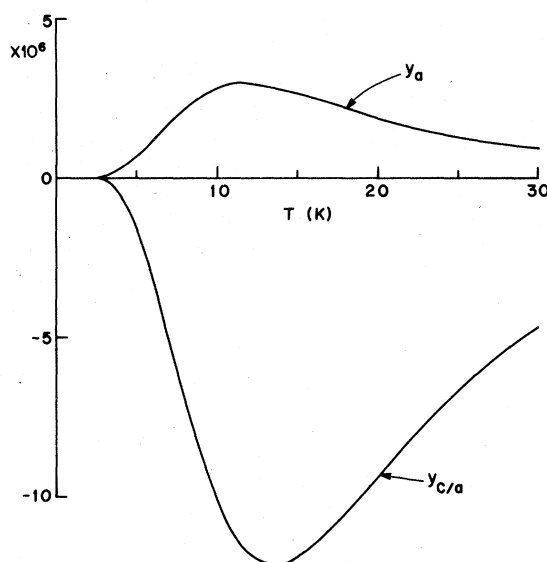
FIG. 9. Plot of y_a vs temperature, when including the strain dependence of all crystal-field amplitudes, and of $y_{c/a}$, when including the strain dependence of all but the B_4^0 amplitude.

$(1/c)\ \partial c/\partial T$ to be negative (as observed), $y_{c/a}$ has to be negative. For $(1/a)\ \partial a/\partial T$ to be positive, y_a has to be either positive or else smaller in magnitude than y_a. Fairly good qualitative agreement with experiment is obtained by calculating the quantity y_a including the contribution of all crystal-field amplitudes, and by calculating the quantity $y_{c/a}$ including all but the B_4^0 amplitude (Fig. 9). These curves would be in reasonable qualitative agreement with the data. For an absolute comparison, we have to await the determination of the elastic constants of the PrNi₅ crystal.

The thermal-expansion calculation has thus shown that at least some of the crystal-field amplitudes have a strain sensitivity different from what one would predict in the point-charge model. It is on the other hand also clear that by choosing the proper strain derivatives of the amplitudes B_n^m, agreement with the thermal-expansion data can be obtained, as shown by the proper position of the maxima in the y_a and $y_{c/a}$ curves. This reinforces our belief, that our proposed crystal-field level scheme for Pr^{3+} in PrNi₅ must be close to the true one since it fits reasonably well the specific-heat, magnetic-susceptibility, as well as the thermal-expansion data. It has come to our attention that the crystal-field levels in PrNi₅ have recently been observed by means of inelastic neutron scattering experiments by Andreeff et al.[13] A fit to their data yields indeed a level scheme very similar to ours, which is most gratifying. For comparison, their eigenvalues are also included in Table I.

[1]J. H. Wernick and S. Geller, Acta Crystallogra. 12, 662 (1959).

[2]E. A. Nesbitt, H. J. Williams, J. H. Wernick, and R. C. Sherwood, J. Appl. Phys. 33, 1674 (1962).

[3]R. S. Craig, S. G. Sankar, N. Marzouk, V. U. S. Rao, W. E. Wallace, and E. Segal, J. Phys. Chem. Solids 33, 2267 (1972).

[4]K. Andres and E. Bucher, J. Appl. Phys. 42, 1522 (1971).

[5]K. Andres, P. H. Schmidt, and S. Darack, in *Proceedings of the 20th Conference on Magnetism and Magnetic Materials, San Francisco, Calif.-1974*, edited by C. D. Graham, Jr., G. H. Landen, J. J. Rhyne, AIP Proc. No. 24, (AIP, New York, 1975).

[6]H. R. Ott, K. Andres, E. Bucher, and J. P. Maita, Solid State Commun. 18, 1303 (1976).

[7]K. Andres and S. Darack, Physica (Utrecht) 86–88,

B, C, 1071 (1977).

[8]N. Marzouk, R. S. Craig, and W. E. Wallace, J. Phys. Chem. Solids 34, 15 (1973).

[9]E. Segal and W. E. Wallace, J. Solid State Chem. 2, 347 (1970).

[10]A. E. Dwight, Trans. Am. Soc. Met. 53, 479 (1961).

[11]M. T. Hutchings, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. XVIII, p. 237.

[12]A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[13]A. Andreef, K. Valter, Kh. Grissmann, L. P. Kaun, B. Lippold, V. Mats, and T. Franznkhaim, 11324 *Joint Institute for Nuclear Research, Dubna, USSR* (1978) Comm. P14–11324 (unpublished).