PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Crystal-field effects in the high-field magnetization of polycrystalline $PrNi_5$

E. Leyarovski and J. Mrachkov
Georgi Nadjakov Institute of Solid State Physics, Sofia, Bulgaria

A. Gilewski and T. Mydlarz
International Laboratory for High Magnetic Fields and Low Temperatures, Wroclaw, Poland

(Received 16 October 1986)

The induced magnetic moment of polycrystalline $PrNi_5$ was investigated at $T=4.2$ K in magnetic fields up to 40 T. The magnetization increases faster than linear in magnetic fields less than 14 T, which is believed to be a result of a level crossing induced by the magnetic field. The observed magnetization compares well with the induced magnetic moment, calculated on the basis of a molecular-field Hamiltonian, which includes the crystalline electric field potential, Zeeman term, and isotropic exchange interactions. The calculations indicate that at lower temperatures the level crossing would give a stepwise increase of the magnetization, which is expected to be between 15 and 19 T, depending on the crystal-field level scheme. At 4.2 K the transition is smeared out and should be very sharp if the temperature is lowered below 1 K.

I. INTRODUCTION

The intermetallic compound $PrNi_5$ crystallizes in the hexagonal $CaCu_5$ structure.[1] The Ni ions are thought to be nonmagnetic or weakly magnetic[2] as a result of the filling of the 3*d* shell with the valence electrons of the Pr ions. Therefore the magnetic properties of $PrNi_5$ are prescribed to the magnetism of the praseodymium ions. The praseodymium ions are placed in lattice points with hexagonal symmetry.

The magnetic susceptibility of polycrystalline $PrNi_5$ shows a weak maximum around 16 K.[3] The lack of a specific-heat anomaly around 16 K led Craig *et al.*[4] to conclude that the anomaly in the susceptibility was a crystalline electric field (CEF) effect, and that the ground state of the Pr ions is a Γ_4 singlet, with a first excited state Γ_5 doublet. The anisotropy in the magnetic susceptibility predicted by this model was opposite to the observed one.[5] The full energy scheme was deduced in (Ref. 5) by fitting the experimental data to the heat capacity and magnetic susceptibility of a monocrystalline sample to a Hamiltonian which includes the CEF potential and a Zeeman term. A very similar CEF energy-level scheme was deduced from the experiments on inelastic neutron scattering[6] (see Table I).

The singlet ground state of the praseodymium ion will remain stable down to very low temperatures only if the value of the exchange interactions between the ions are sufficiently small. In a number of different experiments—magnetic susceptibility[5] and NMR studies on single crystals[7] and the very low-temperature heat capacity of polycrystalline samples[8]—the value of the molecular field exchange constant is estimated to be equal to 0.10 meV. This is several times smaller than the value necessary for an induced magnetic order in the electron system. For this reason $PrNi_5$ was very successfully used in hyperfine-enhanced nuclear magnetic cooling.[8,9]

In this paper we report a study of the induced magnetic moment of $PrNi_5$ at $T=4.2$ K in impulse magnetic fields up to 40 T. The experimental results are compared with the calculated magnetic moment on the basis of a molecular-field Hamiltonian.

II. EXPERIMENTAL

The investigated $PrNi_5$ samples were prepared from powdered Pr with purity 99.9 wt. %, obtained from the Alfa Division of Ventron Corporation Ltd., and powdered Ni with purity 99.999 wt. % obtained from Johnson-Matthey Corp., JM grade 1. Stoichiometric amounts of the above metals were mixed and well homogenized. The mixture was split up in several parts of about 2 g each. They were heated up in Ta crucibles at 1000 K for 15 h. The Ta crucibles were sealed off in quartz ampules with pure argon at a pressure of approximately 200 Torr. The so-reacted mass was sintered and homogenized carefully again. Tablets were produced by cold pressing at room temperature with a 20-ton press. These tablets were arc melted on a water-cooled copper hearth, under an argon atmosphere. The so-produced samples (of about 10 g each) were used as cast, without any additional thermal treatment. From these specimens, used in the investigation of the thermal properties of $PrNi_5$, small pieces were cut for the investigation of the magnetic properties.

The analysis of the samples with an electron probe x-ray microanalyzer type JXA-5A JEOL showed that there was not any unreacted Pr and Ni. The x-ray diffraction verified that the specimens were single phased

TABLE I. Crystalline electric field parameters of $PrNi_5$ (in kelvin).

Reference	B_2^0	$B_4^0\times 10^2$	$B_6^0\times 10^4$	$B_6^6\times 10^2$
5	3.74	4.49	7.70	2.72
6	7.12	5.77	11.81	3.14

and had hexagonal $CaCu_5$-type structure. The lattice parameters were $a = 4.960$ Å and $c = 3.985$ Å, which compares well with the results of other authors.[5,10]

The residual resistance ratio of our specimens is $R_{300}/R_{4.2} = 4$. For comparison the best $PrNi_5$ specimens have a residual resistance ratio 24–32.[11]

Employing a ballistic magnetometer[12] the magnetization at $T = 4.2$ K was measured in magnetic fields up to 14 T, produced by a water-cooled Bitter-type magnet. The accuracy of the measurements was better than 1%. The measurements in impulse magnetic fields up to 40 T were performed with a pulse width of 18 ms for the highest magnetic fields.[13] The magnetization measurements were made using an induction method similar to that described by Allen *et al.*[14] The signal from the pick-up coil, which was proportional to the derivative of the magnetic moment (dM/dt), after integration was registered on the Y channel of a digital recorder. The signal from the magnetic field pick-up coil, proportional to the derivative of the magnetic field (dH/dt), after integration was registered on the other channel of the digital recorder. The curve $M = f(H)$ was displayed on an X-Y recorder. The magnetization was immediately deduced in arbitrary units. The absolute values were obtained by making the initial part of the magnetization curve coincide with the induced magnetic moment of the same sample in stationary magnetic fields.

III. THEORY

The magnetic behavior of the praseodymium ion can be described within the molecular-field approximation by the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{\mathrm{CF}} + \mathcal{H}_{\mathrm{mf}} , \tag{1}$$

where

$$\mathcal{H}_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 \tag{2}$$

is the CEF potential of the Pr ions in hexagonal environment, O_n^m are Stevens operators and B_n^m are the crystal field amplitudes.[15] As pointed out in Refs. 5 and 6, the c/a ratio differs from the ideal, and therefore the crystal field amplitude B_2^0 cannot be taken equal to zero. Moreover the relation $B_6^6/B_6^0 = \frac{77}{8}$ obtained in the point charge model does not hold any more. For these reasons the CEF potential, in this case, is described by four independent crystal field amplitudes.

Two sets of values for the CEF parameters were used in the calculations—those derived in Refs. 5 and 6—and are summarized in Table I. In Table II are given the eigenstates and eigenvalues calculated in Ref. 5 and those derived from the CEF parameters from Ref. 6. It should be noted that although the energy schemes are very similar, the CEF parameters in Refs. 5 and 6 differ. This is a consequence of the fact that in Ref. 5 B_6^0 and B_6^6 are independent variables, while in Ref. 6, the ratio B_6^6/B_6^0 was calculated using the appropriate value of the c/a ratio, i.e., the experimental data in Ref. 5 was fitted with four independent variables, while in Ref. 6 there were only three.

The molecular field term ($\mathcal{H}_{\mathrm{mf}}$) in Eq. (1), is written as

$$H_{\mathrm{mf}} = -g_J \mu_B (\mathbf{H} + \lambda \mathbf{M}) \cdot \mathbf{J} , \tag{3}$$

where $\mathbf{H}$ is the applied magnetic field, $\mathbf{J}$ is the total angular momentum, $\mathbf{M}$ is the induced magnetic moment, and λ is the molecular field constant, connected with the exchange coupling parameters (J_{ij}) between the praseodymium ions:

$$\lambda = \frac{1}{2 g_J^2 \mu_B^2} \sum_{i \neq j} J_{ij} . \tag{4}$$

By considering the explicit form of the eigenfunctions of the Hamiltonian [Eq. (1)] it can be shown that the magnetization will be pointed along the applied external magnetic field. The magnetization is calculated from:

$$\mathbf{M} = g_J \mu_B \langle \mathbf{J} \rangle , \tag{5}$$

where

$$\langle \mathbf{J} \rangle = \frac{\sum_{i=1}^{g} m_i \exp(-e_i / k_B T)}{\sum_{i=1}^{g} \exp(-e_i / k_B T)} ; \tag{6}$$

here m_i are the matrix elements of $\mathbf{J}$ for all the eigenstates of the Hamiltonian [Eq. (1)] and e_i the corresponding eigenvalues. The Hamiltonian [Eq. (1)] was diagonalized numerically and Eqs. (5) and (6) solved self-consistently, using an iteratative procedure for each given value of the magnetic field and temperature.

The magnetization of $PrNi_5$ is anisotropic. Therefore in order to compare the calculated magnetization with the experimental data an averaging has to be done. The following Hamiltonians were considered for magnetic fields parallel and perpendicular to the c axis:

$$\mathcal{H}_{\parallel} = \mathcal{H}_{\mathrm{CF}} - g_J \mu_B (H + \lambda M) J_{\parallel} , \tag{7a}$$

$$\mathcal{H}_{\perp} = \mathcal{H}_{\mathrm{CF}} - g_J \mu_B (H + \lambda M) J_{\perp} ; \tag{7b}$$

here M is the average magnetization, which is assumed to be equal to

$$M = \frac{g_J \mu_B}{3} (2 \langle J_{\perp} \rangle + \langle J_{\parallel} \rangle) . \tag{8}$$

The magnetization of a polycrystalline sample was calculated in the same way as above, but Eq. (8) was also in-

TABLE II. Eigenfunctions and eigenvalues of the Hamiltonian [Eq. (2)] as derived by Andres *et al.* (Ref. 5), $a_2 = 0.214$ and $a_4 = 0.977$, and calculated with the CEF parameters of Andreeff *et al.* (Ref. 6) $a_2 = 0.180$ and $a_4 = 0.984$.

	Eigenfunction	e_i (K) Ref. 5	e_i (K) Ref. 6
Γ_5^1	$a_4 \lvert \pm 4 \rangle + a_2 \lvert \mp 2 \rangle$	332	392.4
Γ_3	$1/\sqrt{2}(\lvert +3 \rangle + \lvert -3 \rangle)$	156.8	158.6
Γ_5^2	$a_2 \lvert \pm 4 \rangle - a_4 \lvert \mp 2 \rangle$	48.2	54.0
Γ_6	$\lvert \pm 1 \rangle$	39.4	39.0
Γ_1	$\lvert 0 \rangle$	22.9	17.6
Γ_4	$1/\sqrt{2}(\lvert +3 \rangle - \lvert -3 \rangle)$	0.0	0.0

cluded in the self-consistent solving of the equations for the induced magnetic moment.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetization of the polycrystalline $PrNi_5$ is shown in Fig. 1. In the same figure are shown the results of the calculated magnetization (as explained in Sec. III) using both sets of CEF parameters. An interesting feature of the experimental data is that for magnetic fields less than 14 T the magnetization increases faster than linear. This is clearly demonstrated on Fig. 2 on which the differential susceptibility is shown. The differential susceptibility $(\partial M/\partial H)$ is calculated by numerical differentiation of the magnetization (experimentally determined and calculated). From Fig. 1 it seems that for the magnetization is better accounted if the CEF parameters derived in Ref. 5 are used. In Fig. 2 the quantitative agreement between the calculated differential susceptibility with the parameters from Ref. 5 and that derived from the experimental data is also better, though the position of the maximum is better predicted with the level scheme from Ref. 6.

Such a behavior of the induced magnetic moment is a result of the crystal field effects, as will be discussed below. First let us consider the case of a magnetic field applied along the c axis. The application of a magnetic field polarizes the ground state to give a pure $|+3\rangle$ state. The maximum magnetic moment of this state is $m_i = g_J\langle +3|J_z|+3\rangle = 2.4\mu_B$/atom (for Pr^{3+} $g_J = 0.8$). In high magnetic fields the energy of this state decreases proportionally to the applied magnetic field and the magnetic moment m_i. One of the excited states (in this case one of the Γ_5^2 states) is polarized in the magnetic field to give a pure $|+4\rangle$ state, with a maximum magnetic moment $m_j = 3.2\mu_B$/atom. The energy of this state decreases proportionally to its magnetic moment, i.e., faster than the energy of the ground $|+3\rangle$ state. So that there exists a magnetic field at which the state $|+4\rangle$ should cross the $|+3\rangle$ ground state, the result being a stepwise increase of the magnetization (if the temperature is sufficiently low so that only the ground state is populated). Calculations with the CEF parameters of $PrNi_5$ (either of those from Refs. 5 or 6) indicate that such a level crossing would occur at very high magnetic fields—of the order of 400 T. The differential susceptibility would have a maximum at the magnetic field at which the two levels cross. This cannot explain the observed behavior of the induced magnetic moment of polycrystalline $PrNi_5$ in magnetic fields around 14 T.

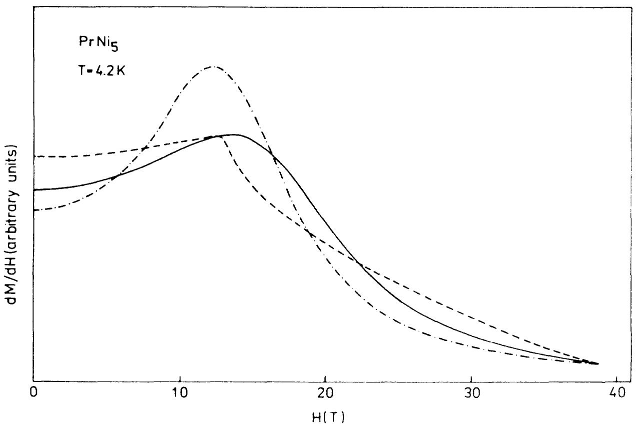

FIG. 2. Differential susceptibility of polycrystalline $PrNi_5$ at $T = 4.2$ K; — — —, calculated from the experimental data; ——, calculated with the CEF parameters of Andres *et al.* (Ref. 5); —·—·—·, calculated with the CEF parameters of Andreeff *et al.* (Ref. 6).

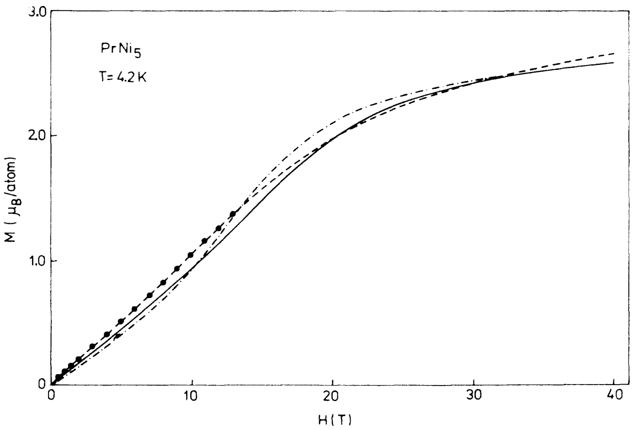

FIG. 1. Induced magnetic moment of polycrystalline $PrNi_5$ at $T = 4.2$ K: ●●●, measured in stationary magnetic fields; — — —, impulse field measurements; ——, calculated with the CEF parameters deduced by Andres *et al.* (Ref. 5); —·—·—·, calculated with the CEF parameters of Andreeff *et al.* (Ref. 6).

Similar behavior of the magnetization of singlet ground state systems was first discussed by Cooper,[16] where the cubic thulium compound TmSb was considered. In Ref. 16 it was predicted that the full magnetic moment of Tm^{3+} ion would be reached stepwise, each step corresponding to a crossing of the ground state by an excited state with a greater magnetic moment, for magnetic field pointed along the hard axis. Tsuneto and Murao[17] considered an effective $S = 1$ system with a singlet ground state. They showed that the level crossing is a second-order phase transition. Polycrystalline $PrNi_5$ cannot be described by an effective $S = 1$ system. Moreover, in order to compare the calculated results with the experimental data all nine states of the Pr ion (for Pr^{3+}, $J = 4$) must be included. The analytical solution, in this case, is easy enough only for magnetic field along the c axis, when the diagonalization of the Hamiltonian [Eq. (1)] is reduced to diagonalization of four matrices, each 2×2. In the case of a magnetic field perpendicular to the c axis, to obtain an analytical expression would mean a diagonalization of one matrix 4×4 and one matrix 5×5, which might not be possible (to obtain an analytical solution). Therefore the diagonalization of the Hamiltonian [Eq. (1)] and the calculation of the induced magnetic moment were done numerically.

The application of a magnetic field perpendicular to the

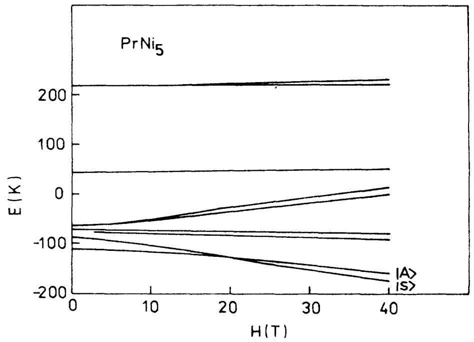

FIG. 3. Calculated energy level scheme of $PrNi_5$ at $T=0.3$ K with the CEF parameters of Andres *et al.* (Ref. 5) as a function of the applied magnetic field, perpendicular to the *c* axis.

c axis admixes excited wave functions into the ground state to give an antisymmetrical wave function ($|A\rangle$). This antisymmetrical wave function is a linear combination of all states $|\pm i\rangle$, $i=1,2,3,4$. The state Γ_1 ($|0\rangle$) is not admixed into the ground state Γ_4 $[1/\sqrt{2}(|+3\rangle-|-3\rangle)]$, because the latter is antisymmetrical. The calculated maximum magnetic moment of the state $|A\rangle$, $m_A=g_J\langle A|J_\perp|A\rangle$ is equal to $2.4\mu_B$/atom (in the limit of extremely high magnetic fields). The magnetic field admixes into the excited state Γ_1 other wave functions to give a symmetrical wave function $|S\rangle$. The maximum magnetic moment of $|S\rangle$ is $3.2\mu_B$/atom, and therefore at a certain magnetic field H_{cr}, $|S\rangle$ should cross the ground state. At this field there should be a stepwise increase of the magnetization, under the conditions mentioned above. The calculated energy level scheme of $PrNi_5$ for a magnetic field perpendicular to the *c* axis using the CEF parameters from Ref. 5 is shown in Fig. 3 for $T=0.3$ K. The expected magnetization of $PrNi_5$ for a magnetic field perpendicular to the *c* axis for temperatures $T=2.0$ K and 0.3 K is shown in Fig. 4(a) (level scheme deduced in Ref. 5) and Fig. 4(b) (level scheme deduced in Ref. 6). The amplitudes of the wave functions $|A\rangle$ and $|S\rangle$ strongly depend on the magnetic field and therefore the increase of the magnetization (equal to the difference of the magnetic moments of the states $|A\rangle$ and $|S\rangle$) also depends on the magnetic field.

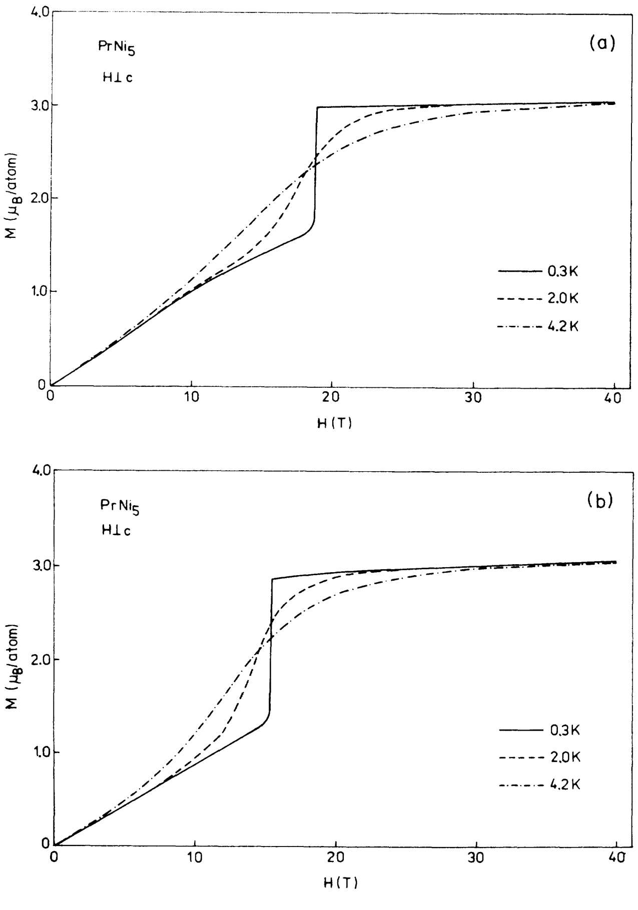

FIG. 4. (a) Calculated induced magnetic moment of $PrNi_5$ for magnetic field perpendicular to the *c* axis with the CEF parameters deduced by Andres *et al.* (Ref. 5). (b) Calculated induced magnetic moment of $PrNi_5$ for magnetic field perpendicular to the *c* axis with the CEF parameters deduced by Andreeff *et al.* (Ref. 6).

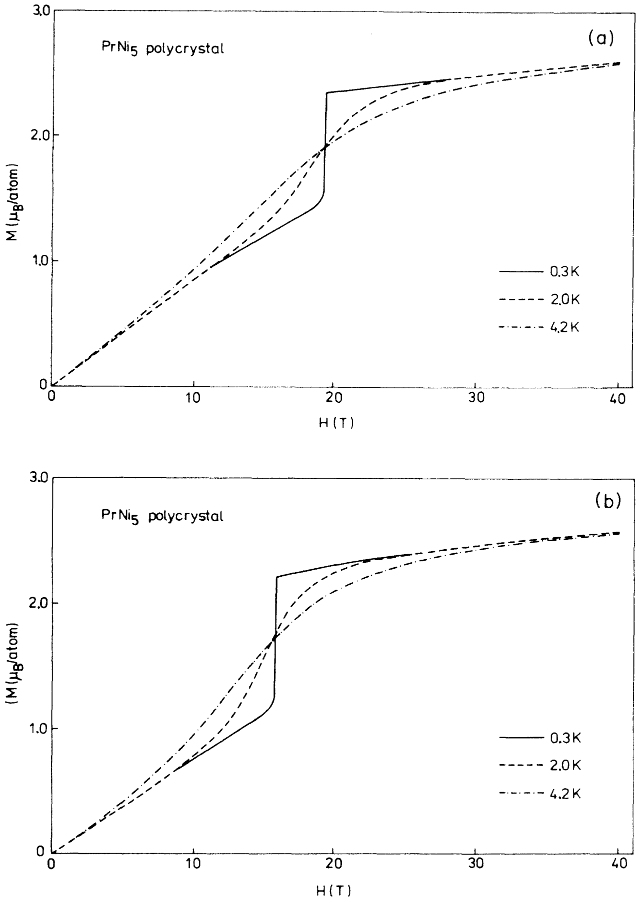

FIG. 5. (a) Calculated induced magnetic moment of polycrystalline $PrNi_5$ with the CEF parameters deduced by Andres *et al.* (Ref. 5). (b) Calculated induced magnetic moment of polycrystalline $PrNi_5$ with the CEF parameters deduced by Andreeff *et al.* (Ref. 6).

TABLE III. Predicted critical magnetic fields (H_{cr}) and rise in the magnetization (ΔM) for monocrystalline (**H**⊥**C**) and polycrystalline samples at $T=0.3$ K.

Sample	CEF level scheme of Ref. 5		CEF level scheme of Ref. 6	
	H_{cr} (T)	ΔM (μ_B/atom)	H_{cr} (T)	ΔM (μ_B/atom)
monocrystalline	18.7	1.18	15.3	1.48
polycrystalline	19.3	0.75	15.8	1.04

The critical magnetic field H_{cr} depends on the CEF splittings and on the amplitudes a_2 and a_4 (Table II). It should be also noted that the full magnetic moment of the Pr ion for magnetic fields perpendicular to the c axis at low temperatures should be reached in relatively moderate fields.

The magnetization of a polycrystalline PrNi_5 at $T=2.0$ K and 0.3 K was calculated with both sets of CEF parameters and the results shown in Figs. 5(a) and 5(b). The predicted critical magnetic moments are higher than those predicted for a monocrystal, because the magnetic moments for **H**‖**C** are smaller than those for **H**⊥**C** and thus using Eq. (8) for the effective magnetic field $H+\lambda M$ acting on the ions in a polycrystal is smaller than the effective magnetic field in a monocrystal for **H**⊥**C**. The full magnetic moment of the Pr ion in a polycrystalline PrNi_5 can be reached only when the full magnetic moment for magnetic fields along the c axis is reached.

The predicted critical magnetic field (H_{cr}) and the corresponding rise of the magnetization (ΔM) for monocrystalline and polycrystalline samples are summarized in Table III for $T=0.3$ K. The increase of the temperature from $T=0.3$ K to $T=4.2$ K would smear out the transition. The region of magnetic fields for which both levels $|A\rangle$ and $|S\rangle$ have appreciable population is about 6 T for $T=4.2$ K, while for $T=0.3$ K this region is less than 0.5 T. Therefore the magnetization at $T=4.2$ K rises only slightly faster than linear (Fig. 1) and there is no abrupt increase.

V. CONCLUSIONS

The induced magnetic moment of polycrystalline PrNi_5 was studied in magnetic fields up to 40 T at $T=4.2$ K. The magnetization in magnetic fields less than 14 T increases faster than linear. This is clearly seen in the field dependence of the differential susceptibility (Fig. 2). We consider this as an experimental evidence of a CEF level crossing induced by the magnetic field.

The induced magnetic moment was compared with the calculated magnetization using a molecular field Hamiltonian, which includes the CEF potential, Zeeman term, and isotropic exchange interactions. The CEF parameters used were those determined in Refs. 5 and 6. The calculations indicate that for monocrystalline samples the full magnetic moment of the Pr^{3+} ion ($3.2\mu_B$/atom), at sufficiently low temperatures, would be reached stepwise for magnetic fields both along and perpendicular to the c axis. For magnetic fields along the c axis the critical magnetic field is estimated to be about 400 T. For magnetic fields perpendicular to the c axis the estimates of the critical magnetic field are 18.7 and 15.3 T for the CEF parameters deduced in Refs. 5 and 6, respectively.

The magnetization of a polycrystalline sample is an average of the magnetization of a monocrystalline sample along the different directions. The transitions in monocrystalline samples must also be present, in some way, in polycrystalline samples, though at slightly different magnetic fields. The behavior of the magnetization of a polycrystalline sample cannot be explained by the transition induced by a magnetic field along the c axis; for this, it would be necessary to have a magnetic field an order of magnitude higher than the one we attained. The observed effect is believed to be the result of a CEF level crossing in the crystallites of the polycrystal for which the magnetic field is perpendicular to the c axis.

The transition at $T=4.2$ K is smeared out and should be very sharp if the temperature is lowered below 1 K. Similar transition was experimentally observed in monocrystalline Pr at 4.2 K,[18] for magnetic field along the c axis. In the case of monocrystalline Pr the energy of the ground state Γ_1 is independent of the applied magnetic field along the c axis. On the other hand, in the case of PrNi_5 the energy of the ground state decreases with the magnetic field. That while the transition would be very sharp if the temperature is below 1 K, when the region of magnetic fields, for which the two levels (ground and excited states) have comparable population, is very small.

---

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

[2] W. E. Wallace, *Rare Earth Intermetallics* (Academic, New York, 1973).

[3] E. A. Nesbitt, H. J. Williams, J. H. Wernick, and R. C. Sherwood, J. Appl. Phys. **42**, 1522 (1971).

[4] R. S. Craig, S. G. Sankar, H. Marzouk, V. V. L. Rao, W. E. Wallace, and E. Segal, J. Phys. Chem. Solids **33**, 2267 (1972).

[5] K. Andres, S. Darak, and H. R. Ott, Phys. Rev. B **19**, 5447 (1979).

[6] A. Andreeff, V. Valter, Kh. Grissmann, L. P. Kaun, B. Lippold, V. Mats, and T. Franzkhaim, Joint Institute for Nuclear Research, Dubna, U.S.S.R., Commun. P14-11324 (1978).

[7] N. Kaplan, D. Ll. Williams, and A. Graeyevski, Phys. Rev. B **21**, 899 (1978).

[8] M. Kubota, H. R. Folle, Ch. Buchal, R. M. Muller, and F. Pobell, Physica B + C **108**, 1093 (1981); M. Kubota, Jülich Report No. 1688 (1980) (unpublished).

[9] K. Andres and S. Darak, Physica B **86-88**, 1071 (1977).

[10] K. H. J. Buschow, J. Less-Common Met. **16**, 4511 (1968).

[11] Private communication of K. A. Gschneidner, Jr. and B. J. Beaudry cited in H. Ishimoto, N. Nishida, T. Furulayashi, M. Shinohara, Y. Takano, Y. Miura, and K. Ôno, J. Low Temp. Phys. **55**, 17 (1984).

[12] T. Mydlarz, Ph.D. thesis, Institute for Low Temperature and Structure Research, Wroclaw, 1977 (unpublished).

[13] A. Gilewski, International Laboratory for High Magnetic Fields and Low Temperatures, Wroclaw, Report No. 40, 1984 (unpublished).

[14] Y. Allen, J. de Gunzbourg, J. P. Krebs, and A. Median, Rev. Sci. Instrum. **39**, 1360 (1968).

[15] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[16] B. R. Cooper, Phys. Lett. **22**, 244 (1966).

[17] T. Tsuneto and T. Murao, Physica **51**, 186 (1971).

[18] K. A. McEwen, G. J. Cock, L. W. Roeland, and A. R. Mackintosh, Phys. Rev. Lett. **30**, 287 (1973).