PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

High-field magnetization of polycrystalline praseodymium

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(Received 29 October 1985; revised manuscript received 22 May 1986)

The field dependence of the induced magnetic moment in polycrystalline Pr is studied in impulse magnetic fields up to 45 T at 4.2 K and in stationary magnetic fields up to 18 T at 20 and 30 K. No anomalies in the magnetization have been observed which might be associated with the metamagnetic phase transition in single crystals at 31.5 T [K. A. McEwen, G. J. Cock, L. W. Roeland, and A. R. Mackinstosh, Phys. Rev. Lett. **30**, 287 (1973)], as well as with any changes of the orientation of the magnetic moments characteristic for an antiferromagnetic. The observed magnetization is satisfactorily described using a molecular field Hamiltonian including the crystal electric field potential, exchange interactions, and Zeeman-effect term.

I. INTRODUCTION

Praseodymium crystalizes in double-hexagonal-close-packed (dhcp) structure, with half of the ions experiencing a local crystal field of approximately hexagonal symmetry (hexagonal ions) while the rest of the ions are in approximately cubic surroundings (cubic ions). The ground state is a nonmagnetic singlet for all the ions, with exchange interactions (only for the hexagonal ions) close to the critical value necessary for spontaneous magnetic ordering in the electron system.[1]

For a number of years there has been a controversy about the existence of a magnetically ordered phase in Pr. In the early neutron diffraction experiments on polycrystalline samples[2] additional reflections to the nuclear reflections of the dhcp structure at 77 K were observed at low temperatures. This was interpreted as a sinusoidally modulated antiferromagnetic structure existing on the hexagonal ions below 25 K. Antiferromagnetic ordering was also found in a polycrystalline rod.[3] Some of the susceptibility measurements[4,5] show an anomaly around 24 K being consistent with the observation made in Refs. 2 and 3. From the results on the electrical resistivity,[6] only under certain conditions, evidence was obtained for the existence of an antiferromagnetic ordering in polycrystalline Pr at 26 K. The specific-heat experiments below 1 K (Ref. 7) also suggest that a magnetically ordered state in polycrystalline Pr persists at even higher temperatures. Recent neutron scattering studies[8] and very-low-temperature specific-heat measurements[9,10] on a great number of a different single crystals, indicate a long-range magnetic order only at the millikelvin region. A careful neutron polarization analysis of the central peak in a single crystal Pr below 25 K,[11] revealed its magnetic nature, though it was assigned to short-range magnetic correlations and is not the origin of the long range magnetic order at millikelvins. A satellite (responsible for the antiferromagnetic order below $T_N \sim 50$ mK) coexists with the central peak up to temperatures of the order of 1 K, but is attributed to very intense long range magnetic fluctuations.[12] The fluctuations of the magnetic moment resulting in the appearance of the central peak and the satellite seems to be a bulk property of pure Pr and cannot be explained in terms of extraneous factors such as impurities or the surface of the specimen.[12]

The induced magnetic moment of Pr in high magnetic fields was measured in fields up to 37 T (Ref. 13) for a single-crystal and in fields up to 8 T (Ref. 14) for a polycrystal. The magnetization of a single-crystal[13] was found to be highly anisotropic and a metamagnetic phase transition was observed at a magnetic field of 31.5 T, applied along the *c* axis. This is believed to be a result of an excited level crossing the ground state.[13,15] The magnetization of a polycrystal in fields up to 8 T was found to be always equal to the average of the magnetization of the single crystal in the basal plane and along the *c* axis.[14]

In the experiments reported here, the magnetization measurements on polycrystalline samples of Pr at 4.2 K have been extended for the first time in magnetic fields up to 45 T, in order to obtain further information about its magnetic properties.

The induced antiferromagnetic phase transition in single crystals at temperatures of several kelvins by uniaxial stress led McEwen *et al.*[16] to the suggestion that the above mentioned discrepancies in the magnetic properties of Pr might be caused by the existence of internal strains in polycrystals resulting from the highly anisotropic contraction. The highly anisotropic thermal expansion is an intrinsic feature of Pr indeed. Thermal expansion measurements[17] indicate a change of c/a ratio in a single-crystal specimen in the liquid helium temperatures range. Therefore it seems impossible to investigate the behavior of a complete strain-free polycrystalline Pr at temperatures below 77 K. On the other hand, at lowest temperatures the magnetoelastic coupling is also highly anisotropic, reflecting the anisotropy in the magnetic susceptibility. Combining the results of Ref. 17 with the magnetostriction data, McEwen[15] pointed out that the susceptibility dependence on the anticipated change of the c/a ratio might be insufficient to account for the magnetic ordering in polycrystalline samples of Pr. Internal strains can also originate in the course of the crystallization of the samples, which could be recovered at sufficiently high temperatures. For this reason we have studied two polycrystalline specimens, one of which was carefully annealed. It is quite clear that the annealed and unannealed samples should contain at least some internal strains resulting from the anisotropic contraction during the cooling process to liquid helium temperatures.

II. EXPERIMENT

The Pr ingots with a purity better than 99.9 wt. % with respect to all metallic elements were obtained from ALFA Division, Ventron Corporation Ltd. The main impurity was Nd (<0.1 wt. %). The interstitial elements (H, C, N, and O) were not checked. The samples were spark cut from these ingots. During the cutting they were immersed in diffusion pump oil. One of the specimens was wrapped in tantalum foil, sealed off under vacuum (approximately 2×10^{-6} Torr) in a quartz tube and annealed at about 1060 K ($\sim0.9T_{\mathrm{melting}}$) for 100 h. Finally, this sample was cooled down to room temperature at a rate of 10 K/h. Before the annealing and also before every experiment the samples were etched in 10% nitric acid in order to remove oxides which are inevitably formed on the surface. X-ray diffraction measurements were performed by a Dron-2.0 diffractometer, using Cu $K\alpha$ radiation, the reflections being between 5° and 95° (2θ). This x-ray analysis of both specimens verified the DHCP structure of α-Pr only, with crystal lattice parameters $a=3.664$ Å and $c=11.784$ Å, i.e., with ratio $c/2a=1.608$. The x-ray diffraction picture of the annealed sample showed a few additional lines, which were ascribed to PrC_2 and verified by an electron probe x-ray microanalyzer. The source of the PrC_2 is probably the spark cutting process carried out under oil and followed by a diffusion of the PrC_2 in the volume of the specimen in the course of the annealing.

The specimens were also examined by optical microscopy in a 90° polarized light with a Zeiss NU-2 microscope. The typical microstructural changes as a result of the annealing process are illustrated in the photomicrographs (Fig. 1). It is clear from them that in the annealed specimen a significant recrystallization and crystallites growth was realized. Also, from this analysis, the concentration of the PrC_2 is evidently very small, in accord with the results of the electron-probe scanning x-ray microanalysis. Nevertheless, it was not possible to give a definite answer to the question whether the polycrystalline sample of Pr was improved in the annealing process (i.e., whether it became less strained) on the basis of our x-ray and micrography investigations. The interplanar lattice spacings measurements, performed in our x-ray diffraction experiments did not show any distinguishable differences between the annealed and unannealed specimens. It is open to question whether a standard strain gauge method of stress measurement can be applied in this case to estimate the strains in the samples, because it would be necessary to have a compensating gauge mounted on a substrate with the same thermal expansion coefficient as the sample under investigation. On the other hand, evidence for recrystallization of the annealed specimen was reflected in other physical properties e.g., the residual resistivity decreased, the $R_{300\ \mathrm{K}}/R_{4.2\ \mathrm{K}}$ ratio increasing from 8 for the unannealed sample to 11 for the annealed one. No change was observed in both these values at repeated measurements. As it is well known, the $R_{300\ \mathrm{K}}/R_{4.2\ \mathrm{K}}$ ratio is usually one of the best characteristics of the physical purity of metals. It should be noted that even in the purest rare-earth metals available, the electron mean free path is usually limited to a value several orders of magnitude lower than has been achieved for many other metals.[6,15] We would like to also emphasize the role of applied stresses or generated internal strains can play on impurity segregation to grain boundaries and to dislocation lines inside the specimen. The essential difference in very-high-field magnetization of both annealed and unannealed polycrystalline Pr will be discussed in Sec. III.

Employing a ballistic magnetometer,[18] the magnetization at 4.2, 20, 30 K was measured in magnetic fields up to 18 T, produced by a water-cooled Bitter-type magnet. Higher temperatures were obtained by the aid of two heaters, placed above and below the sample holder, and temperatures were measured by a Chromel-gold-iron (Au–0.04 at. % Fe) thermocouple. The stabilization of the temperature was better than 0.25 K for temperatures higher than 4.2 K. The overall accuracy of the magnetic measurements was better than 1%. The measurements in pulsed magnetic fields up to 45 T were performed only at 4.2 K, with a pulse width of 10 ms for the highest fields.[19] The magnetization was 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 obtained in stationary magnetic fields up to 18 T.

III. RESULTS AND DISCUSSION

The magnetization data for both specimens is shown in Fig. 2 ($T=4.2$ K) and Fig. 3 ($T=20$ K and $T=30$ K). Our experimental results compare well with the results of other authors[14] in fields up to 8 T. As expected the magnetic field induces a large magnetic moment, e.g., in field of 45 T the induced magnetic moment is $2.4\mu_B$/atom. This is still smaller than the free ion moment $-3.2\mu_B$/atom. Over the whole range of magnetic fields, the magnetic moment induced in the annealed sample is smaller than that induced in the unannealed one with the difference being much less pronounced at higher temperatures, i.e., $T=20$ K and $T=30$ K. Even at 4.2 K this difference is not significant, but it definitely is larger than the experimental error and systematically increases with the magnetic fields. At the highest fields, the magnetization for the annealed specimen approaches the theoretical curve, obtained by model calculations which are discussed later. One can conclude that the annealing process did not produce any drastic changes in the magnetic properties of the Pr samples under investigation. The difference between the magnetization for the annealed and unannealed samples could not be accounted for by the presence of less than 1% of a nonmagnetic PrC_2, which would result in a smaller decrease of Pr ions. A more probable explanation is suggested by the optical micrography, that in the annealed sample crystallites have some preferred growth along the *c* axis of crystallites which was parallel to the applied magnetic field. Clearly, such an effect should be less pronounced at higher temperatures (see Fig. 3). It was pointed out in Ref. 6 that the anomaly in the electrical resistivity of polycrystalline Pr at 26 K disappears if the specimen was thermally cycled between room and liquid helium temperature, or if the experimental data were taken after a certain time from the annealing. There is no other evidence for such a relation between the annealing and the magnetic properties of polycrystalline Pr. The high field magnetization behavior at 4.2, 20, and 30 K of our annealed sample did not change in the experiment carried out immediately after the annealing as well as after several cooling processes to 4.2 K.

The magnetization of polycrystalline Pr at 4.2 K is not a linear function of the magnetic field, and, at the highest fields reached in our experiments, shows typical behavior

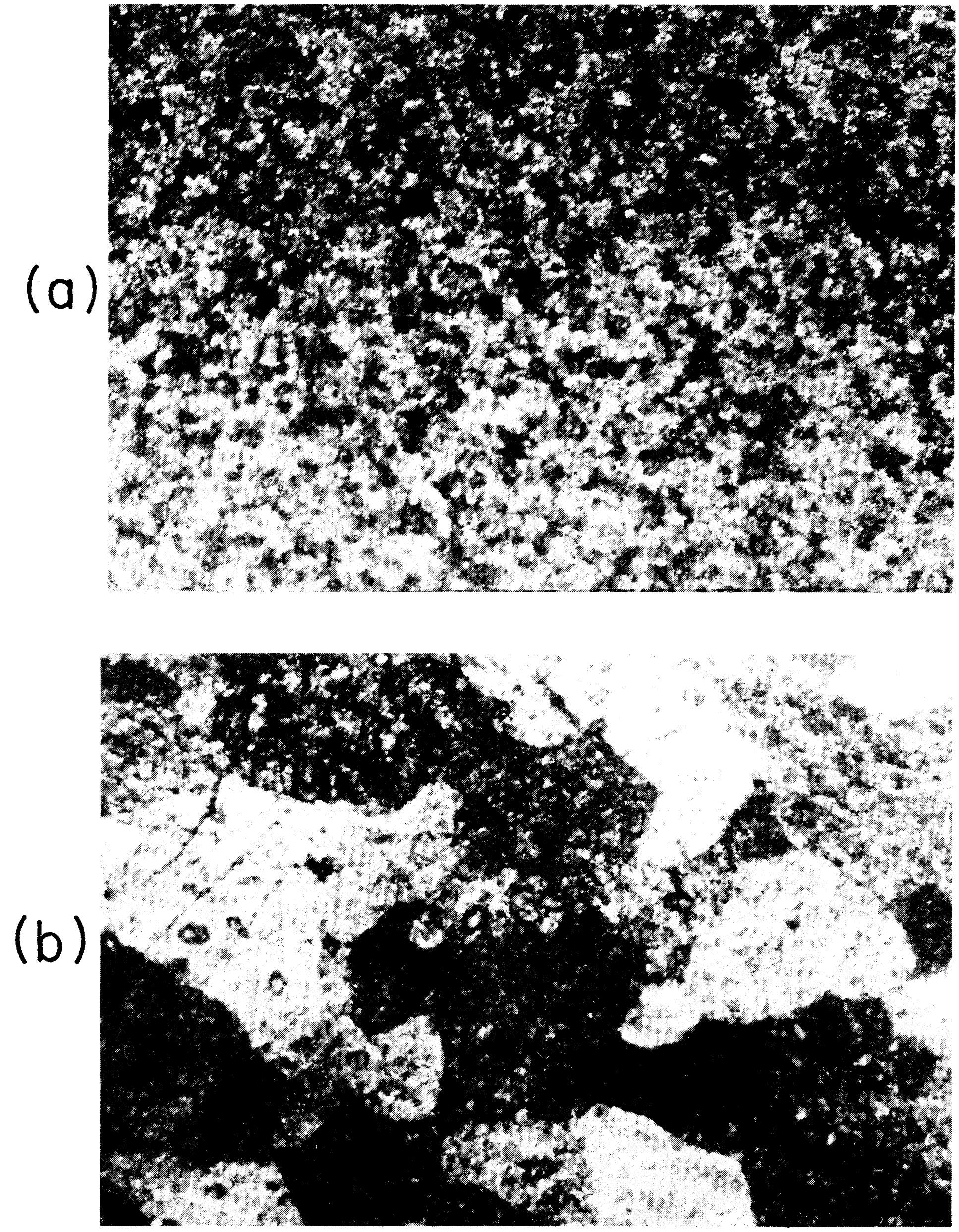

FIG. 1. Photomicrographs (enlarged 1092 times) of the surface of (a) unannealed and (b) annealed specimen of polycrystalline Pr etched in 10% nitric acid.

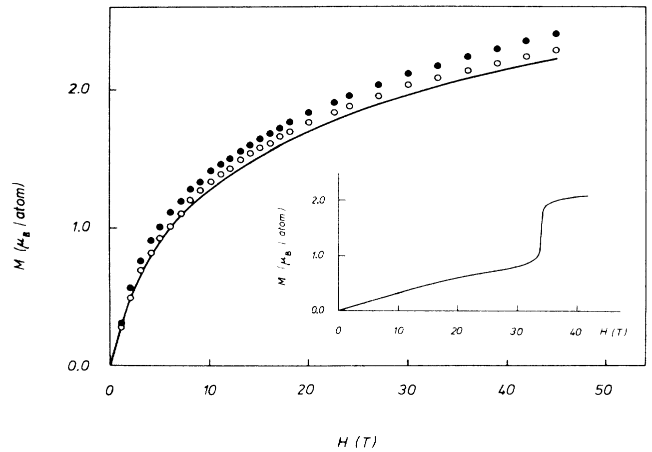

FIG. 2. Magnetization of polycrystalline Pr at 4.2 K. ○, annealed sample; ●, unannealed sample. Solid lines represent calculated results as explained in the text. In the inset calculated magnetization for a single-crystal, for magnetic field along the c axis.

expected for a singlet ground-state system. The relation for calculating the induced magnetic moment of a polycrystal from the induced magnetic moments along the different directions of a single crystal, proposed in Ref. 14 holds in magnetic fields up to 28 T. In fields up to 45 T, no discontinuities in the magnetization have been observed which might be associated either with the metamagnetic phase transition in single crystals at 31.5 T (Ref. 13) or with any changes of the orientation of the magnetic moments in an antiferromagnet. The field dependence of the induced magnetic moment at 20 and 30 K is also characteristic of Van Vleck paramagnets. At these temperatures, the magnetization is not a linear function of the magnetic field, in agreement with the observation of other authors in lower magnetic fields.[14]

The magnetization of polycrystalline Pr can be described phenomenologically using a molecular field approximation and considering the following Hamiltonian for the hexagonal and cubic ions, respectively (see for example Ref. 20):

$$\mathcal{H}(h)=B_{20}(h)O_2^0+B_{40}(h)O_4^0+B_{60}(h)O_6^0+B_{66}(h)O_6^6 -g_J\mu_B\mathbf{H}_{\mathrm{MF}}(h)\cdot\mathbf{J}\ , \tag{1a}$$

$$\mathcal{H}(c)=B_{40}(c)(O_4^0+20\sqrt{2}O_4^3) +B_{60}^{(c)}\left[O_6^0-\frac{35}{\sqrt{8}}O_6^3+\frac{77}{8}O_6^6\right]-g_J\mu_B\mathbf{H}_{\mathrm{MF}}(c)\cdot\mathbf{J}\ . \tag{1b}$$

The O_l^m are Stevens operators,[21] $\mathbf{J}$ is the total angular momentum of the ion, and $\mathbf{H}_{\mathrm{MF}}(h)$ and $\mathbf{H}_{\mathrm{MF}}(c)$ are the sum of the external magnetic field and the magnetic field produced by the surrounding ions, respectively. The values of the crystal field parameters $B_{lm}(h)$, $B_{lm}(c)$ used are those determined in Ref. 1. Hereafter the two-ion couplings, both isotropic and anistropic, considered in Ref. 1 are neglected. According to Ref. 1, the magnetic field acting on the hexagonal ions can be written as

$$\mathbf{H}_{\mathrm{MF}}(h)=\mathbf{H}+\frac{1}{(g_J\mu_B)^2}(\mathcal{J}_{hh}\boldsymbol{\mu}^h+\mathcal{J}_{hc}\boldsymbol{\mu}^c)\ , \tag{2}$$

where $\mathbf{H}$ is the applied external magnetic field, $\boldsymbol{\mu}^h$ and $\boldsymbol{\mu}^c$ are the magnetic moments induced on the hexagonal and cubic ions, respectively, $\mathcal{J}_{hh}$ is the effective exchange parameter between the hexagonal ions, and $\mathcal{J}_{hc}$, between the hexagonal and cubic ions. The molecular field, acting on the cubic ions is obtained in a similar way, assuming that $\mathcal{J}_{hc}=\mathcal{J}_{ch}$ and denoting the effective exchange parameter between the cubic ions by $\mathcal{J}_{cc}$. In this calculation of the induced magnetic moments, all the excited states within the lowest multiplet $^3H_4$ of Pr are included.

The calculated magnetization of a polycrystalline sample involves an average of the magnetization over the different directions. For the hexagonal ions there is a considerable difference between the magnetic moments induced by a field along the c axis and in the basal plane.[13] The anisotropy of the induced magnetic moments on the cubic sites in a DHCP lattice (for $\mathcal{J}_{hc}=0$) is much less pronounced, i.e., it should be less than 10% even in a field of 60 T. If the exchange parameter $\mathcal{J}_{hc}$ is taken into account, the anisotropy in the induced magnetic moments on the hexagonal ions leads to a greater anisotropy in the magnetization of the cubic ions. The induced magnetic moments for the hexagonal and cubic ions were assumed to be, respectively,

$$\mu(h)=\tfrac{1}{3}\mu_{\parallel}^h+\tfrac{2}{3}\mu_{\perp}^h\ , \tag{3a}$$

$$\mu(c)=\tfrac{1}{3}\mu_{\parallel}^c+\tfrac{2}{3}\mu_{\perp}^c\ , \tag{3b}$$

where $\mu_{\parallel}^h$, $\mu_{\parallel}^c$ are the induced magnetic moments for a magnetic field parallel to the c axis, and $\mu_{\perp}^h$, $\mu_{\perp}^c$ for a magnetic field in the basal plane. When calculating the induced magnetic moments for both types of ions, $\boldsymbol{\mu}^h$ and $\boldsymbol{\mu}^c$ in the expressions for the molecular field are replaced by $\mu(h)$ and $\mu(c)$ (defined in (3a) and (3b) for all directions

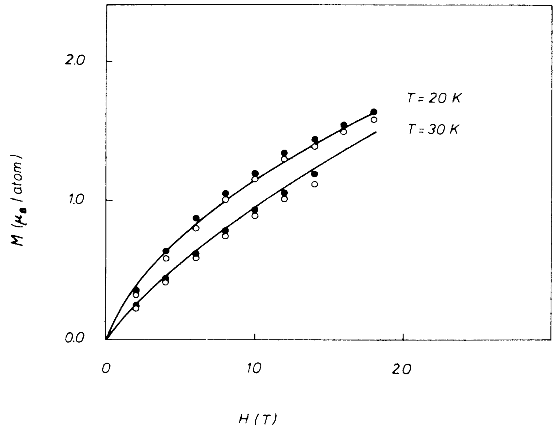

FIG. 3. Magnetization of polycrystalline Pr at 20 K and 30 K. ○, annealed sample; ●, unannealed sample. Solid lines represent calculated results as explained in the text.

of the magnetic field. The diagonalization of the Hamiltonian for the hexagonal and cubic ions, as well as the solutions of the equations for the induced magnetic moments were done self consistently, using an iterative procedure. The total magnetic moment is calculated as

$$M=\tfrac{1}{2}[\mu(h)+\mu_c(h)] \; . \tag{4}$$

The calculations were done using the set of values for the effective exchange parameters which includes those derived in[1] i.e., $\mathcal{J}_{cc}=0.14$ meV and $\mathcal{J}_{hc}\equiv\mathcal{J}_{ch}=0.19$ meV. The value of $\mathcal{J}_{hh}$ was chosen to be equal to 0.17 meV which is 0.96 times the critical value necessary for induced long-range magnetic order.[22] The results of the calculations for polycrystalline samples are plotted in Fig. 2 (solid line). Fitting the experimental data is better for the annealed sample, reflecting some more appropriate conditions for the above described averaging. The results of such a phenomenological treatment for a single crystal, for magnetic field along the *c* axis are presented in the inset of Fig. 2. The calculated critical magnetic field along the *c* axis for the magnetic phase transition in single-crystal Pr is reduced from 36 T (Ref. 1) to 34 T. This transition apparently disappears in polycrystalline samples. Our calculations indicate that as a result of the decrease of the molecular field Eq. (2) acting on the hexagonal ions, it would occur at higher magnetic field—near 48 T. The magnetization was calculated in the same way for temperatures of 20 and 30 K. The obtained results are shown in Fig. 3 (solid lines).

IV. CONCLUSIONS

In conclusion our experiments on the high field magnetization do not confirm the existence of a spontaneous magnetically ordered phase in polycrystalline Pr at temperatures equal to or higher than 4.2 K, regardless of the existence of at least some strains in both annealed and unannealed samples due to the highly anisotropic contraction. It turned out that a magnetic field of the order of 45 T cannot induce in polycrystal the metamagnetic phase transition due to the crossing of the ground state by an excited level, observed in single crystal at $H=31.5$ T and $T=4.2$ K by McEwen *et al.*[13]

The phenomenological description of such a behavior of polycrystalline Pr, using the molecular field approximation, in which the crystalline electric field potential and the isotropic exchange interaction are included, seems satisfactory if the value of the effective exchange parameter between the hexagonal ions is close to the critical value necessary for a spontaneous magnetic order in the electron system ($\eta\sim0.96$).[22] The decrease of the effective field acting on the hexagonal ions due to the averaging of the induced magnetic moment in a polycrystal should lead to an increase of the critical magnetic field for the metamagnetic phase transition up to 48 T. On the other hand, as was shown by McEwen *et al*,[13] the metamagnetic phase transition persists into Pr-Nd alloys, indicating that the crystal field at the Pr sites is only slightly altered by the addition of Nd up to 5.6 at. %. The phase transition persists into the alloy system even at concentrations up to 27 at. % Nd, being only displaced to lower magnetic fields, which just the opposite, might reflect an increase of the molecular field, due to the presence of Nd. So that our high field experiments should be insignificantly affected by less than 0.1 wt. % Nd, present in our specimens.

The broad peak appearing in the neutron diffraction experiments[11,12] is interpreted by Eriksen *et al.*[10] as an ordered state, based on the substantial reduction of the nuclear entropy at $T\simeq T_N$. Our experiments do not confirm this in polycrystals at least up to 45 T. It is not known whether the character of the neutron diffraction results would be the same in such high magnetic fields. Even if the two neutron diffraction peaks, i.e., central peak and satellite, are connected with spin fluctuations[12] with the latter being suppressed in such high magnetic fields.

We believe that there is no fundamental difference in the magnetic properties if polycrystalline and monocrystalline Pr. Their behavior in high magnetic fields is most probably determined mainly by the crystal field effects. A self-consistent treatment in a molecular field approximation which includes these effects as well as sufficiently strong exchange interactions can give an adequate phenomenological description of the magnetic properties of both modifications. It seems that the predicted critical magnetic field for the metamagnetic phase transition in polycrystal ($\sim$48 T) to be reasonable. Nevertheless it is worth emphasizing the essential role of the internal strains in the low-temperature behavior of the strongly magnetostrictive, light rare-earth elements.[16] Naturally, in our molecular field calculations an ideally isotropic, free of any strains, lattice is assumed. But as it was yet pointed out it seems impossible to make experiments with a completely strain-free polycrystalline Pr at temperatures below 77 K. That while it is not excluded that the predicted metamagnetic phase transition in polycrystalline Pr may occur at some different magnetic field that the predicted above 48 T. Experiments for the investigation of Pr in magnetic fields higher than 50 T and at temperatures lower than 4.2 K are in progress.

ACKNOWLEDGMENTS

The authors are indebted to Dr. E. Popov for help with the computer calculations, to Dr. I. Vassilev for the x-ray studies of the specimens, and to Professor I. Gutzov for the microphotography.

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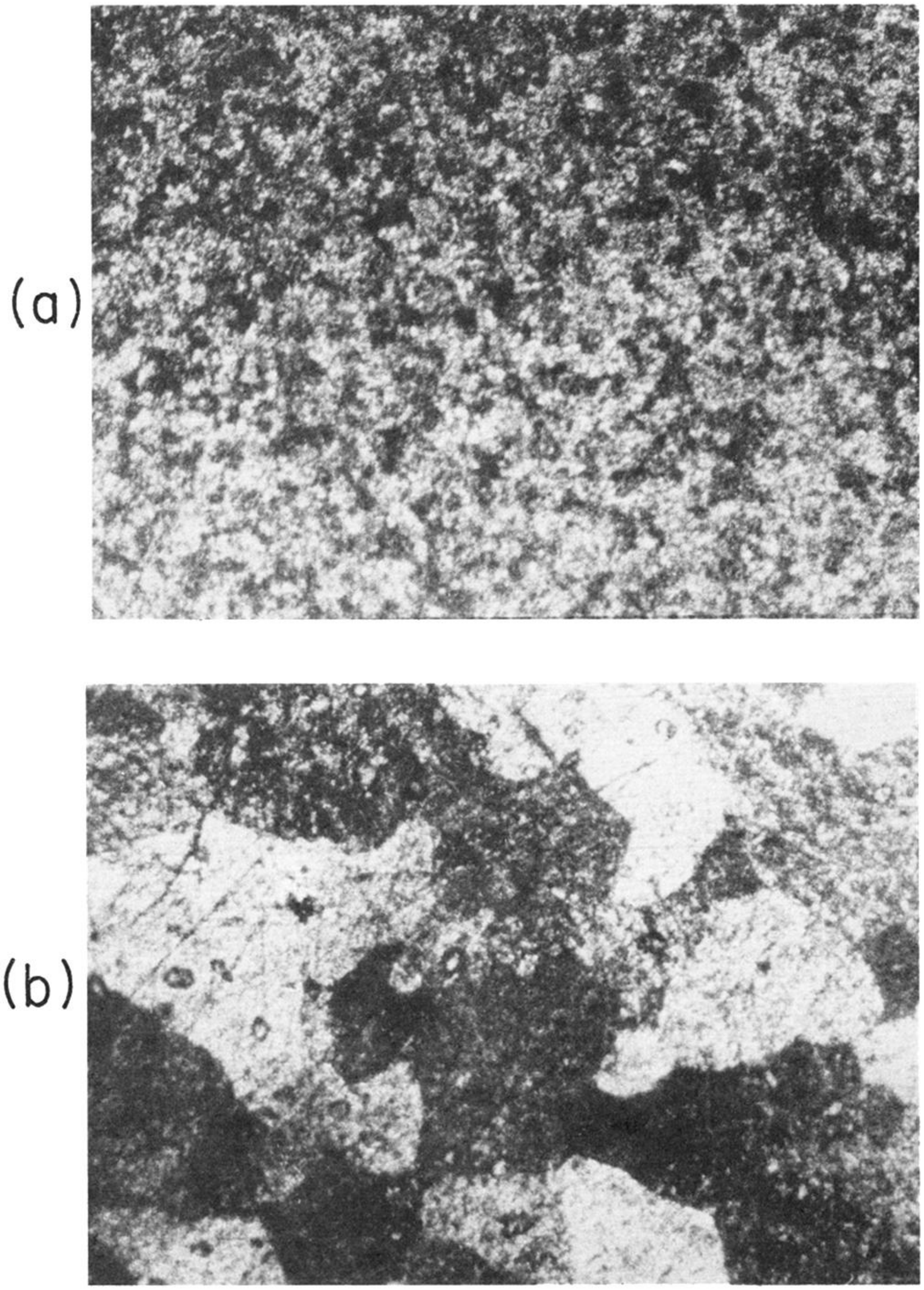

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