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ANTIFERROMAGNETISM OF PRASEODYMIUM*

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The rare earth metals, in general, exhibit the behavior of tripositive ions embedded in a sea of conduction electrons. Magnetic susceptibility measurements[1] suggest this description for Pr metal since the observed effective moment is that appropriate for the $^3H_4$ ground state of the Pr^{+3} ion. The susceptibility exhibits a departure from Curie-Weiss behavior below 100°K and becomes temperature independent below about 5°K. The heat capacity measurements of Parkinson, Simon, and Spedding[2] showed low-temperature anomalies for Ce, Pr, and Nd. For Ce and Nd these were λ-type anomalies and were associated with cooperative magnetic effects. This interpretation was later verified by neutron diffraction observations.[3,4] For Pr, the anomaly, which reached a maximum at about 30°K, was quite broad and was attributed to the thermal population of the electronic states produced by crystal-field splitting of the $4f$ levels. More recently the nuclear hyperfine coupling contribution to the heat capacity has been extracted from low-temperature measurements.[5-7] This term is only about 1/30 of that calculated[5,8-10] for Pr on the assumption of an exchange field sufficiently large to produce the full ordered moment appropriate to the tripositive ion. This has been taken as an indication of the absence of magnetic order in Pr even though it has not been possible to account satisfactorily for the observed nuclear hyperfine contribution on that basis. It is the purpose of this note to report some neutron diffraction observations on metallic Pr which show the existence of antiferromagnetic order for this material.

Neutron diffraction data were obtained between room temperature and liquid helium temperatures for two different polycrystalline samples of Pr. Both were commercially available samples, one from Lindsay Chemical Company and the other from Michigan Chemical Corporation. Spectrographic analysis relative to other rare earth impurities showed 97+% purity for the Lindsay sample and 99.3+% purity for the Michigan sample. The similarity in the neutron diffraction results for both samples indicates that the observed antiferromagnetic behavior is an intrinsic property of the metal and not to be associated with impurities. This behavior is illustrated in Fig. 1 which shows neutron diffraction patterns obtained at 77°K and at 1.4°K. In the 77°K pattern only those nuclear reflections attributable to the double hexagonal close packed structure of Pr are present, and the intensities of these reflections are in accord with that structure. The additional reflections observed at lower temperatures are apparent in the 1.4°K pattern. The $\sin\theta/\lambda$ values of these reflections are close to, but slightly displaced from, those of the (001) and (003) reflections of a magnetic unit cell with twice the c-axis dimension of the chemical unit cell. For both reflections the displacement is to higher $\sin\theta/\lambda$ values. A similar pattern was observed for Nd, the adjacent rare earth in the periodic table with the same crystal structure, for which

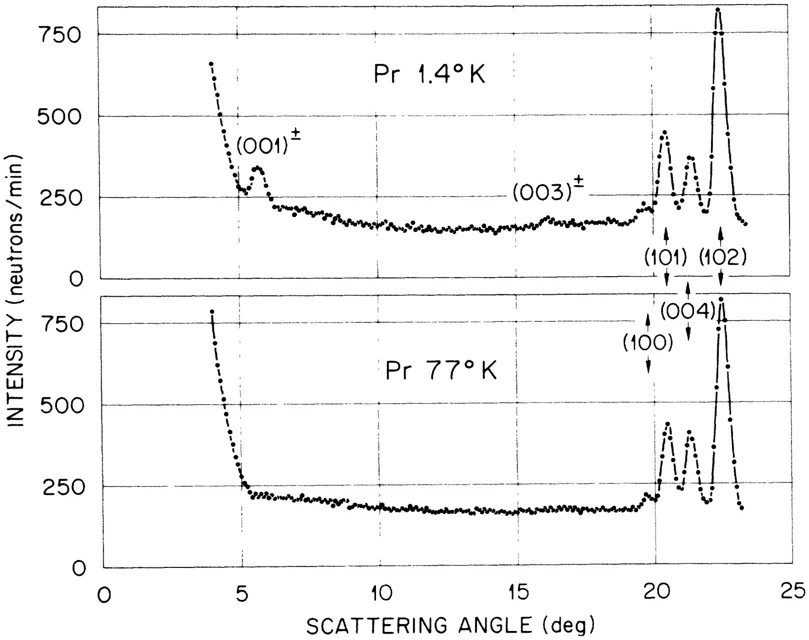

FIG. 1. Neutron diffraction patterns of polycrystalline Pr metal at 77°K and at 1.4°K.

the magnetic structure was recently determined from single-crystal measurements.[4] In that magnetic structure, alternate hexagonal layers of moments were aligned antiparallel but there was a superimposed sinusoidal modulation of the moments in the b_1 direction. The magnitude of the modulation wave vector was about $0.12b_1$ for the hexagonal site moments and $0.15b_1$ for the face-centered cubic site moments. If a similar moment configuration is assumed for Pr, then the observed displacement of the reflections from the (001) and (003) positions corresponds to a modulation wave vector of $0.13b_1$. In the absence of the single-crystal data needed for verification, it is tentatively suggested that the magnetic structure of Pr is similar to that of Nd. The magnetic reflections in Fig. 1 are indexed accordingly.

The magnetic intensities were internally calibrated from the nuclear intensities using the scattering amplitude 0.44×10^{-12} cm for Pr. If the Nd-type structure is assumed, then these observed intensities correspond to a maximum moment of 0.7 μ_B per Pr in the event that all moments are ordered and to 1.0 μ_B if only those moments located at hexagonal (or face-centered cubic) sites are aligned.

The intensity of the $(001)^{\pm}$ reflection was observed between 1.4°K and the Néel temperature of 25°K. There was no intensity variation between 1.4 and 4.2°K and therefore no indication of a magnetic structure change to be associated with the heat capacity anomaly at 3.2°K reported by Lounasmaa.[7] The absence of a λ-type specific-heat anomaly corresponding to the Néel transition at 25°K remains unexplained. This might be smeared out by a larger thermal repopulation effect, or perhaps revealed by a more careful examination in the 25°K region. The observed antiferromagnetic order probably accounts for the nuclear hyperfine contribution to the low-temperature specific heat. As was mentioned previously, the observed effect is only about 1/30 of that calculated on the assumption that the expectation value of J_z attains the maximum J value for the free ion. The neutron diffraction results show that the full moment of 3.2 μ_B per atom does not develop. On the basis of the Nd-type structure, the maximum of the modulated moment distribution is only 0.7 μ_B for ordering of all moments and 1.0 μ_B if only one half of the moments order. Recognizing the quadratic dependence of the specific-heat coefficient on $\langle J_z\rangle$,[5,8-10] and that because of the sinusoidal modulation $\langle\mu^2\rangle = \frac{1}{2}\mu_{\max}^2$, these ordered moment values correspond, respectively, to 1/40 and 1/20 of the maximum contribution in fairly good agreement with the observation.

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CURRENT OSCILLATIONS AND COLLECTIVE WAVES IN CdS

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This Letter describes a new type of oscillatory behavior of electron currents flowing in CdS under conditions where the electron drift velocity exceeds the velocity of sound. The frequencies of these oscillations are not determined by the transit time of sound through the sample alone, as reported by earlier investigators,[1,2] but also depend sensitively upon the voltage applied to the crystal, the electron density, and the ambient temperature of the crystal. These oscillations are believed to arise from the coupling between long-wavelength collective phonon waves[3,4] and mobile electrons.

The observations described here were made on photoconducting CdS crystals which were insulating in the dark ($\rho > 10^9$ Ω-cm). Electrical contact to the CdS was made with indium, and the current flow was in the basal plane of the crystal. Voltage pulses between 10 μsec and 100 μsec in duration were applied to samples whose lengths ranged between 4 to 16 mm. The oscillations reported here occurred only if sufficient voltage was applied to the crystal to produce sonic amplification. Under these conditions, the sample was observed to emit maxima of acoustic noise in the 10- to-100-Mc/sec frequency band simultaneously with minima in the current.

The oscillations of present interest (type I) differ from those previously described by McFee[2] (hereafter called type II) in several important respects. The period of the type-II oscillation was equal to $2(L/v_S)$ where v_S is the velocity of the amplified sound modes, and L is the length of the crystal. This period is substantially independent of any intensive property of the crystal. In contrast, the longest observed period for the type-I oscillations was about $1.7(L/v_S)$. Further, the period of type-I oscillations could be substantially changed by varying the electron density,

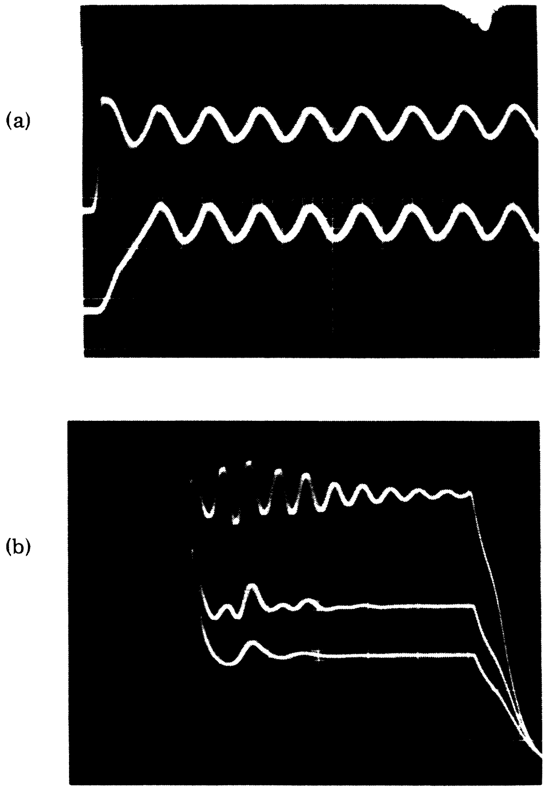

FIG. 1. (a) Current oscillations in a CdS sample. Top trace was recorded with rise time of voltage pulse of 0.2 μsec; lower trace was recorded with rise time of 4.0 μsec. Note that oscillations have same amplitude and frequency (about 250 kc/sec) in both traces. (b) Modal shift in current oscillations in a CdS sample with fixed applied voltage. Increasing the electron density from about $10^{13}/\text{cm}^3$ (lowest trace) to about $2 \times 10^{13}/\text{cm}^3$ (upper trace) has caused the appearance of the second harmonic frequency (about 400 kc/sec).