

4.2°K (1,a), 20°K (1,b), and 30°K (1,c) in the case of a field acting along the [111] axis. A negative-resistance section is clearly seen; it turns into a plateau at 30°K and vanishes with further increase of temperature. In the case of liquid-helium temperature, the carriers were produced by weak constant illumination in the main absorption region. The abrupt increase of the current at 10 V/cm corresponds to the start of the impurity breakdown. At higher experimental temperatures, no constant illumination was used. At 20°K there is a section of periodic instability, occurring in the region 2 - 8 V/cm. An oscillogram of the oscillations is shown in Fig. 2. The frequency of the oscillations corresponds approximately to the ratio of the carrier drift velocity to the sample length. At 4.2°K the increase of the illumination intensity led to a decrease of the depth of the negative section and to the appearance of current oscillations. The oscillations had frequently an irregular character.

Uniaxial compression along the field direction led to a sharp decrease of the maximum on the current-voltage curve (Fig. 3). At a pressure 200 - 300 kg/cm² (at T = 4.2°K) the negative section disappears completely. Such changes can be readily explained from the point of view of the investigated effect, since a pressure in the [111] direction splits the conduction band into three valleys and one [3], and when the field and compression directions coincide the lowest energy position is assumed by the "cold" valley, in which the electrons accumulate in the absence of a field. In this case the carrier heating does not lead to an increase of the resistance.

When the field acts along the [100] axis (this is not accompanied by a change in the valley population), no singularities are observed on the current-voltage characteristic.

Thus, the results of the experiment offer evidence that the observed effect is due to intervalley redistribution of the electrons as they become heated.

In conclusion, the authors thank L. E. Vorob'ev for help with the experiment and for a discussion of the results.

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ANOMALOUS TEMPERATURE DEPENDENCE OF SPIN DENSITY IN PrF₃ SINGLE CRYSTALS

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Submitted 18 April 1968
ZhETF Pis'ma 7, No. 12, 451-454 (20 June 1968)

During the course of an investigation of a number of paramagnetic single crystals, we observed an unusual temperature dependence of the shift of one of the components of the NMR of F¹⁹ in single-crystal PrF₃.

Whereas lowering of the temperature of the previously-investigated paramagnets leads only to an increase of the total width of the spectrum, leaving the relative positions of the components unchanged, in the case of PrF₃ the position of one of the components relative to the remaining lines in the NMR spectrum of F¹⁹ varies continuously with temperature.

Figure 1 shows the temperature dependence of the positions of the maxima of the components of the NMR spectrum of F^{19} in single-crystal PrF_3 . The field H_0 is oriented along the x direction (which in turn is perpendicular to the threefold axis and coincides with the direction a of the unit cell of the crystal, whose structure is of the LaF_3 type [1]). The presence of five components at low temperatures and of two at higher ones is connected with the presence in the PrF_3 crystal of the structurally-nonequivalent fluorine ions F_I , F_{II} , and F_{III} and their diffusion [2,3].

As seen from the figure, the maxima of the four components shift linearly with changing $(T + \theta)^{-1}$, where T is the absolute temperature and $\theta = 51.5^\circ$ is the Weiss constant for PrF_3 . This linear variation is connected with the fact that the position of the components in the NMR spectrum of F^{19} is determined by the local magnetic field that acts on the nuclei and is proportional to the macroscopic susceptibility χ [4]. Consequently the linear dependence obtained for these components is simply a consequence of the Curie-Weiss law:

$$\chi = C/(T + \theta).$$

In the general case the local magnetic field in the crystal is the sum of the dipole component h_{dip} (due to the magnetic fields of the paramagnetic ions Pr^{3+}) and the hyperfine component h_{hf} [5]. The appearance of h_{hf} at the F^{19} nuclei in the PrF_3 crystal is due to the transfer of the spin density from the Pr^{3+} to the F^- ions as a result of a mixing of the states of these ions. The unusual behavior of the fifth component of the F^{19} NMR spectrum can be explained by assuming that not the ground state but the excited state of the Pr^{3+} ion takes part in this case in the mixing of the states. The spin density of the unpaired electrons F_I is then proportional to the population of the excited level, i.e., to $\exp(-\Delta E/kT)$,

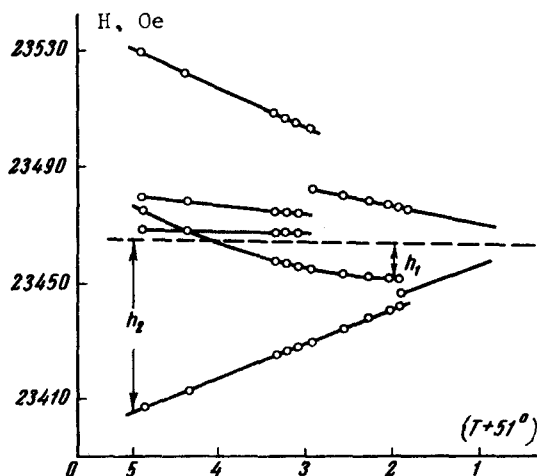


Fig. 1. Temperature dependence of the positions of the maxima of the components of the NMR spectrum of F^{19} in single-crystal PrF_3 . The dashed line indicates the position of the center of gravity of the spectrum.

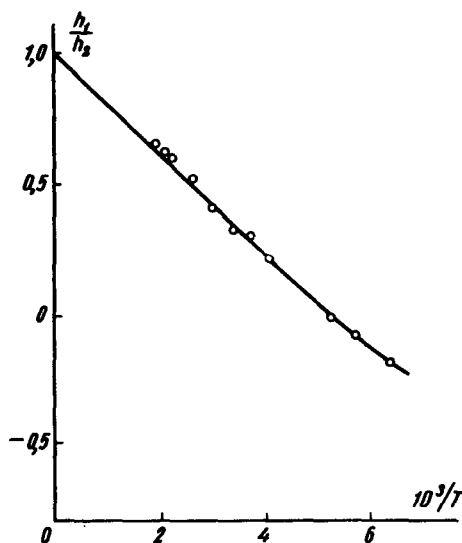


Fig. 2. Ratio of local fields at the structurally-nonequivalent nuclei F_I and F_{II} .

where ΔE is the energy difference between the excited and ground levels. The total local field h_1 acting on the F_I nucleus is:

$$h_1 = h_{\text{dip}} + h_{\text{hf}} = h_{\text{dip}} + D \exp(-\Delta E/kT),$$

where $D = h_{\text{hf}}$ if $T \rightarrow \infty$.

As already noted, the local fields (and their components) are proportional to $\chi = C/(T + \theta)$. By taking the ratio of the local fields h_1 and h_2 acting on the structurally nonequivalent nuclei F_I and F_{II} , we automatically exclude their dependence on the susceptibility χ . Inasmuch as for F_{II} , as seen from Fig. 1, we have $h_2 = P\chi$ (where P does not depend on T), we get

$$h_1/h_2 = A + B \exp(-\Delta E/kT),$$

where A and B are constants that do not depend on T . For high temperatures, when $kT \gg E$, we can write

$$h_1/h_2 \approx A + B(1 - \Delta E/kT).$$

Figure 2 shows a plot of h_1/h_2 against $1/T$, calculated on the basis of the data of Fig. 1. As seen from the figure, this dependence is nearly linear in the entire investigated temperature region (up to -120°C). We can regard our assumptions as correct and attribute the unusual variation of the shift of one of the components of the NMR spectrum of F^{19} in PrF_3 to the part played by the excited states of the unpaired $4f$ electrons in the formation of partially covalent bonds between the Pr^{4+} and F^{19} atoms. The linear temperature dependence of h_1/h_2 allows us to estimate that $\Delta E < 100 \text{ cm}^{-1}$.

It is of interest to note that spectroscopic investigations of PrF_3 point to the presence in this crystal of a low-lying excited unpaired-electron state with $\Delta E = 66 \text{ cm}^{-1}$ [6].

In conclusion we note that the observed phenomenon depends strongly on the orientation of the magnetic field relative to the crystal. When the magnetic field is oriented along the threefold axis, the temperature dependence of the NMR spectra of F^{19} in the PrF_3 crystal has no singularities compared with other paramagnets. The described effect is observed only when the magnetic field is applied to the crystal at a certain angle to the threefold axis, the maximum deviation taking place when H_0 is perpendicular to this axis. This can mean that the "population" of the excited state is the result of a superposition of the ground and excited states under the influence of the magnetic field. In other words, the symmetry of the wave functions of the excited and ground states is such that their superposition is possible only with the aid of the magnetic-moment projection operator [7].

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