EPR in Single Crystals of NiBr₂

J. S. Wells and D. R. Winder*
National Bureau of Standards, Boulder, Colorado

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Previously reported EPR measurements1 on NiBr₂ gave a single value and linewidth for the resonance in powdered material. We have made EPR measurements on single crystals of NiBr₂ as work preliminary to a possible antiferromagnetic resonance experiment. The nickel bromide crystals were grown2 from sublimed vapor in the presence of water vapor and helium on a glassy substrate at approximately 600°C. The transparent, dark yellow samples crystallized as dendrites, whiskers, and platelets.

The platelets used in this experiment were approximately 2 mm in the planar dimension and about 0.01 mm thick. Optical measurements showed a broad transmittance minimum at 0.81 μ and complete absorption between 0.42 and 0.34 μ, the lower limit of the measurement.

NiBr₂ belongs to the CdCl₂ class of hexagonal layered structures which have symmetry 3m. The layered structure consists of the bromine ions in a face-centered-cubic array with the nickel ions occurring in sheets normal to a body diagonal and inserted between every second layer of bromine ions. Under a crystalline field of this symmetry, the orbital ground state of Ni²⁺ is split into A₁g, A₂g, and Egü levels. The lowest of these levels is triply degenerate in spin. A spin-orbit interaction of this same symmetry should produce two levels, A₁g and Egü, for the spin states, and hence could produce two lines when a magnetic field is applied. We have observed only a single line, presumably because the dipole–dipole interaction masks the possible A₁g–Egü splitting. A single line corresponds to an effective spin S' = 5. Our g values are to be interpreted in terms of an effective spin Hamiltonian.

We have made measurements at 300° and 76°K and have attempted measurements at 4°K, well below the Néel temperature of 60°C. At 300°K, we find a slightly anisotropic g factor, with g₁₁ = 2.19 ± 0.02 and g₄ = 2.21 ± 0.02. The lines are nearly equal in intensity. Representative linewidths are ΔH₁ = 800 G and ΔH₁₁ = 1000 G, where ΔH is the distance between extrema in the derivative of the absorption. As the temperature is decreased, the anisotropy in the g factor increases as does that in the linewidths. At 77°K, g₁₁ = 2.16 ± 0.01 and g₄ = 2.23 ± 0.01. Typical linewidths here are ΔH₁₁ = 600 G and ΔH₄ = 400 G. The absorption derivatives at 77°K are shown in Fig. 1. An experiment was also made to check for a possible sixfold anisotropy in the basal plane and no anisotropy was detected. An antiferromagnetic resonance experiment, however, could provide a considerably more sensitive means of detecting small anisotropy. At 4°K, the resonance was not observed within the range of the spectrometer which was limited to 24 kG.

Since g₄ is larger than g₁₁ we conclude that an easy plane rather than an easy axis exists for the preferred spin direction in the crystal. Linewidth calculations were made using Van Vleck’s dipole–dipole broadening...
expression,
\[ h^2(\Delta \nu)^2 = \frac{1}{2} S(S+1)g^4a^4 \sum \frac{[1 - 3 \cos^2 \theta]}{r_b^4}, \]

taking sums out to third-nearest nickel ions in the basal plane. The calculated values were about 1000 G when the spins were assumed to lie in the basal plane. Some exchange narrowing and compensating lifetime broadening are necessary to account for the decrease in linewidth at 77°K.

Our measurements were made using a conventional K-band spectrometer operating in the 23.5-GHz region. The frequencies were determined by a wavemeter calibrated by NBS. A commercially available fluxmeter and frequency counter were used to determine the magnetic field strength. An AFC circuit locked the klystron to the cavity frequency. Field modulation at 100 kHz was detected using a phase detector. The derivative signal was displayed on an X-Y plotter, which had the X axis coupled to the field-sweep drive. The boiling points of the refrigerants at this altitude were taken as the temperatures.

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* Permanent address: Colorado State University, Fort Collins, Colo.
1 Y. Ting and D. Williams, Phys. Rev. 82, 507 (1951).