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EPR in Single Crystals of $NiBr_2$

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PREVIOUSLY reported EPR measurements[1] on $NiBr_2$ gave a single value and linewidth for the resonance in powdered material. We have made EPR measurements on single crystals of $NiBr_2$ as work preliminary to a possible antiferromagnetic resonance experiment. The nickel bromide crystals were grown[2] 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.

$NiBr_2$ belongs to the $CdCl_2$ class of hexagonal layered structures which have symmetry $\bar{3}m$. 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 Ni^{2+} is split into A_{1u}, A_{2u}, and E_u levels. The lowest of these levels is triply degenerate in spin. A spin–orbit interaction of this same symmetry should produce two levels, A_{1u} and E_u, 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 A_{1u}–E_u splitting. A single line corresponds to an effective spin $S'=\frac{1}{2}$. 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°K. At 300°K, we find a slightly anisotropic g factor, with $g_{\parallel}=2.19\pm0.02$ and $g_{\perp}=2.21\pm0.02$. The lines are nearly equal in intensity. Representative linewidths are $\Delta H_{\perp}=800$ G and $\Delta H_{\parallel}=1000$ 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, $g_{\parallel}=2.16\pm0.01$ and $g_{\perp}=2.23\pm0.01$. Typical linewidths here are $\Delta H_{\parallel}=600$ G and $\Delta H_{\perp}=400$ 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 $g_{\perp}$ is larger than $g_{\parallel}$ 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

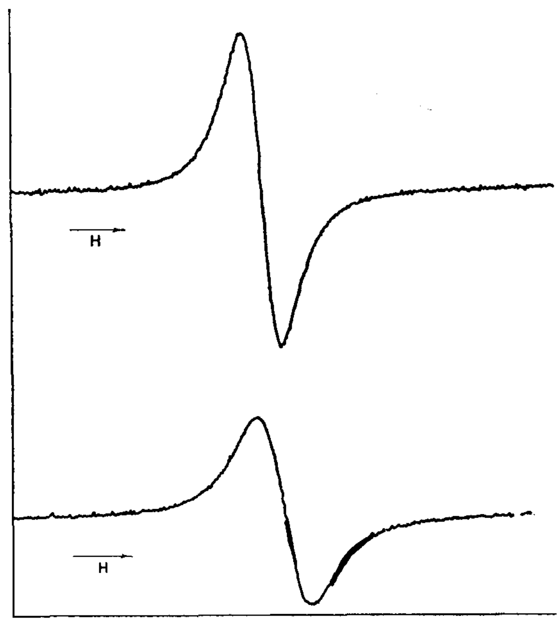

FIG. 1. The derivative of the $NiBr_2$ paramagnetic resonance line at 77°K versus magnetic field shows the anisotropy in g value, linewidth, and intensity. The upper trace corresponds to H_0 in the basal plane and the lower trace corresponds to H_0 parallel to the c axis.

expression,

$$h^2(\Delta\nu)^2=\tfrac{3}{4}S(S+1)g^4\beta^4\sum_k[(1-3\cos^2\theta)/r_{jk}^3]^2,$$

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 commerically 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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