Optical and Magneto-optical Study of the Magnetic Phase Diagram and Incommensurate Magnetic Phase of $NiBr_2$ and $Ni_{1-x}Zn_xBr_2$

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The variations of the 6000 Å band system with temperature from 4.2 to 30 K and magnetic fields up to 3 T applied parallel to the basal plane have been used to map the magnetic phase diagram of $NiBr_2$ and $Ni_{1-x}Zn_xBr_2$ ($x = 0.05, 0.08$). For $NiBr_2$ precise measurements are also reported of the temperature dependence of the wavelength of the two sharp exciton–magnon lines near 6080 Å, and of their behaviour in magnetic fields up to 16 T applied parallel to the *c*-axis and their polarisation.

$NiBr_2$, with the $CdCl_2$ crystal structure, is unique among the metamagnetic transition metal dihalides, and probably among all magnetic materials, in undergoing a transition from a collinear magnetic structure to an incommensurate helical structure with a propagation length which is a smooth function of temperature.[1–3] Early evidence for this phase transition and the existence region of the new phase as a function of temperature and magnetic field came from studying the variation of a pair of sharp electric-dipole absorption lines near 6000 Å.[4] Experiments on the 6000 Å lines were also reported by Giordano *et al.*[5] who examined the effect on them of magnetic fields applied parallel to the *c*-axis. In this paper we give evidence for the polarisation of these lines and the way their intensity and wavelength varies with temperature and magnetic fields applied both parallel and perpendicular to the *c*-axis.

From the theoretical work of Rastelli *et al.*[6] it seems clear that the incommensurate phase is stable because of competition between the near-neighbour ferromagnetic exchange and antiferromagnetic second- and third-near-neighbour exchange, so the magnetic order should be peculiarly susceptible to changes in the lattice, for instance by doping with non-magnetic ions. We have shown that substituting 8% Zn has the effect of reducing the Néel and commensurate–incommensurate transition temperatures and, more remarkably, of completely disordering the propagation direction of the helical phase, while leaving its propagation length only slightly changed.[7] This paper describes how Zn doping changes the dependence of the optical properties on temperature and magnetic field strength, and enables us to determine a magnetic phase diagram for comparison with that obtained by neutron diffraction.

EXPERIMENTAL

The crystals of $NiBr_2$ and $Ni_{1-x}Zn_xBr_2$ were grown by the Bridgman–Stockbarger method, as described in our earlier paper.[7] They cleave readily perpendicular to the *c*-axis so most of the optical experiments were performed with the incident light along the *c*-axis. However, it proved possible to polish one specimen of $NiBr_2$ parallel to this axis, and so record spectra

in σ- and π-polarizations in addition to axial polarisation. Attempts to incorporate more than a nominal 10 mol % Zn resulted in polycrystalline boules, so we report spectra for nominal 5 and 10% doped samples only. The compositions of the slices actually used were 5.5 and 7.7% as determined by atomic absorption spectroscopy.

Absorption spectra were recorded with a McPherson RS10 double-beam spectrophotometer containing a 1 m Czerny–Turner scanning monochromator and prism predisperser. Slits were normally set at 30 μm, giving a spectral bandpass of *ca.* 0.3 cm^{-1}. To monitor the very small changes in wavelength of some of the bands with temperature and applied fields, a refractor plate, driven by a General Scanning repetitive scan unit, was employed. For experiments in zero field an Oxford instruments CF100 continuous-flow helium cryostat and temperature controller were employed while for the magneto-optical experiments the sample was placed in a Thor Cryogenics split-coil superconducting magnet regulated by a Thor type 3011 temperature controller. In this case the spectrophotometer was operated in the logarithmic single-beam mode. Magneto-optical experiments up to 17 T were also carried out using pulsed field equipment at the H. C. Ørsted Institute in Copenhagen. In this instrument, a field pulse obtained by discharging a capacitor bank through a small copper coil immersed in flowing helium gas is synchronized to a light pulse from a xenon flash lamp, dispersed by a 1 m grating monochromator. The resulting spectrum is displayed on an optical multichannel analyser vidicon tube, digitized and plotted. We are most grateful to Dr. I. Trabjerg for access to this equipment, and for his help in operating it.

RESULTS

$NiBr_2$

Fig. 1 shows the three polarised absorption spectra of $NiBr_2$ at 4.2 K in the region of the 6000 Å band. In thin samples the most prominent feature in this region is the intense band between 5980 and 6030 Å which both we[4] and Giordano *et al.*[5] assigned as a phonon sideband of a transition whose electronic origin is near 6100 Å. It has nearly the same intensity in all three polarisations, as do the broad but weaker bands to shorter wavelength (5965 and 5880 Å) which may also be phonon
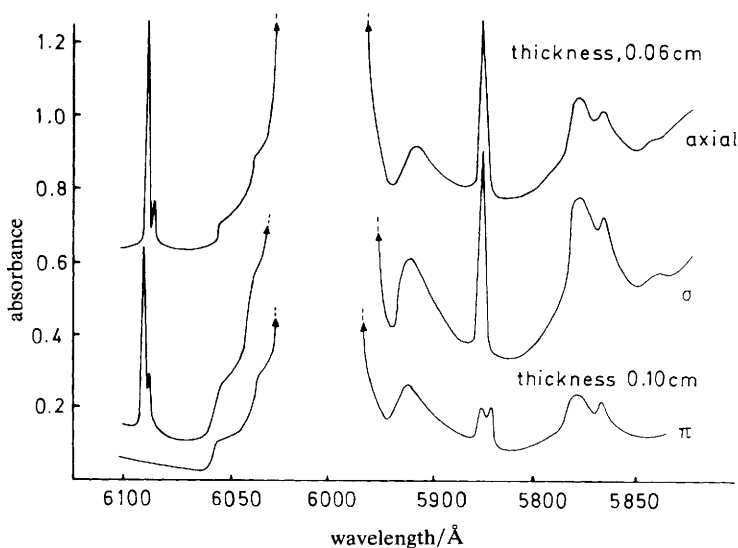

FIG. 1.—Polarised absorption spectrum of $NiBr_2$ at 4.2 K in the 6000 Å region.

sidebands. Two features in the band system, however, have very marked polarisations. At 6080.6 and 6082.6 Å are the pair of very sharp lines (A and B) whose magnetic-field and temperature variation were examined previously, while between 5920 and 5930 Å we find a single very sharp line in axial and σ-polarisation which is replaced by a pair of much weaker lines (5922 and 5927 Å) in π-polarisation. From fig. 1 it is clear that the 6080.6 and 6082.6 Å bands are totally absent from the spectrum when the electric vector E is parallel to the crystallographic c-axis but appear with more or less equal intensity in both the other spectra where $E \perp c$. Since the crystal is optically uniaxial this is sufficient to demonstrate that the bands are allowed by the electric-dipole mechanism, solely with the electric vector within the basal plane.

With increasing temperature, bands A and B move steadily together, at the same time decreasing in intensity, as shown in fig. 2(i). Using the refractor plate to ensure wavelength reproducibility one sees from fig. 2(ii) that between 8 and 20 K the more
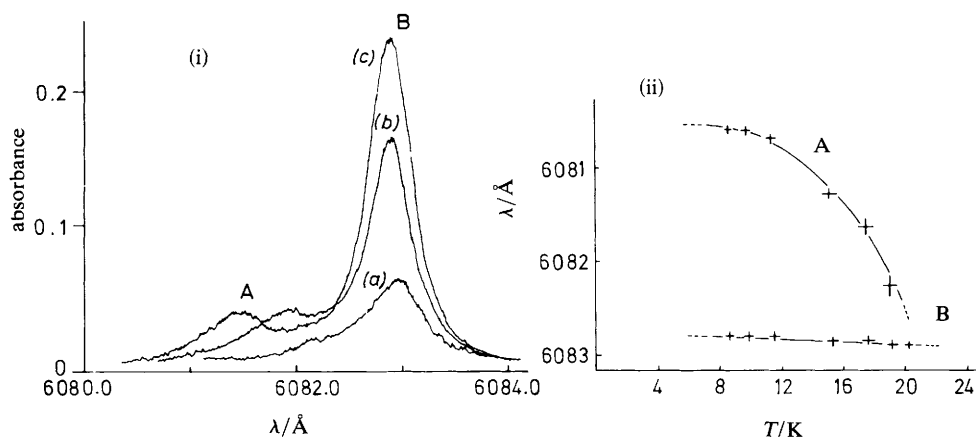

FIG. 2.—The sharp bends A and B in the axial spectrum of NiBr$_2$ as a function of temperature: (a) 20.4, (b) 15.5 and (c) 8.5 K.

intense of the two bands (B) remains almost fixed in wavelength (actually it shifts 0.1 Å to longer wavelength) while the weaker band A shifts towards it. Extrapolating to higher temperatures it appears that the two bands would coincide close to the transition temperature from the incommensurate to the commensurate magnetic structure. The combined areas of the two bands also evolve in a similar way (fig. 3), falling sharply with rising temperature to vanish finally between 22 and 23 K. When a field is applied parallel to the basal plane the two bands vary in the same way with temperature as before, but they now disappear at a lower temperature (e.g. 12 K at 2.4 T). This serves to map the existence region of the incommensurate phase in the (H, T) plane, though a more precise method is to plot isotherms of the band intensity as a function of field, as in our earlier paper.[4] From fig. 3 we also see that the band intensity does not fall uniformly with increasing temperature, but rather it remains nearly constant till ca. 16 K and then drops sharply towards the transition point.

While the effect of a magnetic field parallel to the basal plane is to 'switch off' bands A and B at a value of the field which decreases uniformly with increasing temperature, when the field is applied parallel to the c-axis they remain up to very
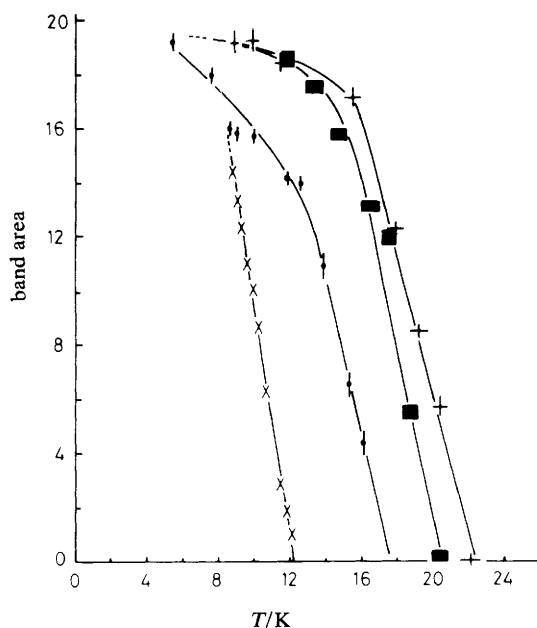
FIG. 3.—Combined areas of bands A and B as a function of temperature: +, $NiBr_2$, 0.0 T; ■, $NiBr_2$, 1.0 T; ×, $NiBr_2$, 2.4 T; ●, $Ni_{0.92} Zn_{0.08} Br_2$, 0.0 T.

high fields. Giordano et al.[5] showed that under these conditions the weaker of the two bands (A) split into a pair while the more intense one did not. However, their data only extended to 3 T and we have repeated the $H\|c$ spectra in pulsed fields up to 15 T. We confirm that the weak band A splits but at higher fields its two components lose intensity and cannot be followed. The intensity of band B also falls, but it shows no splitting, even at the highest fields. As shown in fig. 4, however,
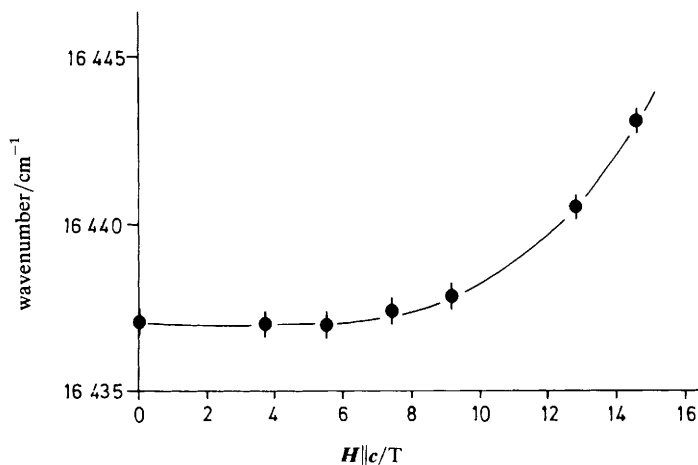
FIG. 4.—Variation of band A with magnetic field parallel to c at 6 K.

above 8 T it begins to shift to higher energy, and continues to do so increasingly: at 15 T it has shifted 6 cm^{-1}.

$$Ni_{1-x}Zn_xBr_2$$

Substitution of up to 8 mol % Zn into the $NiBr_2$ lattice causes no significant changes in the broad intense band at 6000 Å, confirming our assignment of it to a phonon sideband. On the other hand bands A and B, which are less than 1 Å wide in $NiBr_2$, become much broader and coalesce into a single band as seen in fig. 5,
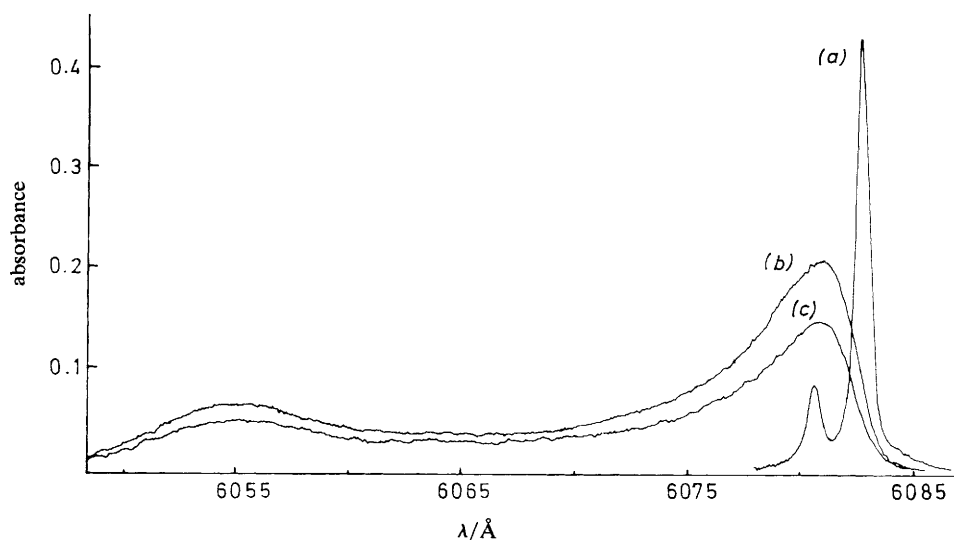

FIG. 5.—Axial absorption spectra at 4.2 K of (a) $NiBr_2$, (b) $Ni_{0.945}Zn_{0.055}Br_2$ and (c) $Ni_{0.92}Zn_{0.08}Br_2$.

where the absorbance of three crystals with zero, 5.5 and 7.7 mol % Zn is normalized to a crystal thickness of 0.8 mm. The band in the doped crystals is quite asymmetric and may consist of two components as in the pure crystal. If so, both lie *ca.* 3 Å to longer wavelength than in the pure crystal, but with no further shift from 5.5 to 7.7% doping. The temperature variation of this broadened band is shown for the 7.7% doped crystal in fig. 3, from which its similarity with the undoped crystal is clear, though its intensity drops to zero at a much lower temperature (17.9 ± 0.6 K compared with 22.5 ± 0.5 K).

As in $NiBr_2$, fields applied parallel to the basal plane of $Ni_{1-x}Zn_xBr_2$ cause the 6080 Å band to lose intensity and finally disappear. Fig. 6 shows the intensity of the band in the 7.7% doped sample, normalized to unity at zero field. At each temperature the intensity remains constant up to a certain value of the applied field, and then falls linearly to zero over a range of *ca.* 0.3 T. Plotting the field $H_{\frac{1}{2}}$ at which the intensity is halved as a function of temperature leads to the phase diagram in fig. 7. In the same figure we show the transition temperature as a function of field for the 7.7% doped crystal determined[7] by neutron diffraction. Agreement between the optical and neutron diffraction values is satisfactory.
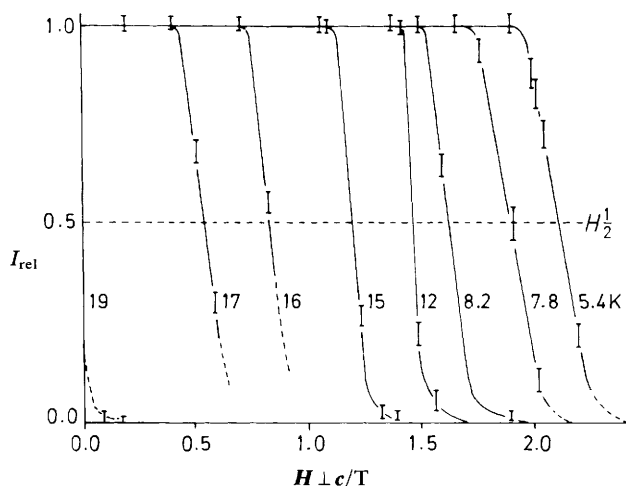
FIG. 6.—Intensity of band A in $Ni_{0.92}Zn_{0.08}Br_2$ (normalized to zero field) as a function of magnetic field perpendicular to c, for various temperatures.

DISCUSSION

The absorption band system between 5980 and 6030 Å in $NiBr_2$ (fig. 1) originates from a spin-forbidden ligand field transition from $^3A_{2g}$ either to $^1T_{2g}$ (our earlier assignment[4] on the basis of agreement with the $3d^8$ Tanabe–Sugano diagram) or to ^1E_g, as preferred by Giordano et al.[5] Such transitions decrease the spin projection of the crystal but, in a magnetically ordered lattice, can become electric-dipole-allowed if the Frenkel exciton created by absorbing a photon is coupled to the simultaneous creation of a compensating spin deviation (spin-wave or magnon) within the electronic ground state. To preserve the $\Delta k \approx 0$ selection rule for photon absorption, the creation of an exciton with a wavevector $+k$ is paired with the creation of a magnon with wavevector $-k$. As is well-known[8] the shape of the resulting profile of absorption plotted against frequency ω (the band shape) is determined by summing such pairs over the Brillouin zone, i.e. by convoluting together the densities of states $N(\omega)$ of the exciton and the magnon. Dealing with weak transitions in inorganic crystals it is customary to assume that the frequency dispersion $\omega_e(k)$ of the exciton can be ignored (i.e. the corresponding density of states is an infinitely sharp line) so the absorption line-shape is determined by the magnon density of states alone, weighted by a wavevector-dependent transition probability.

Exciton–magnon combination bands of this kind are usually relatively wide, some 30–50 cm^{-1} halfwidth being typical. This is because the energy difference between zone-centre and zone-edge magnons is of the order z_1J_1S, where z_1 is the number of near neighbours, J_1 the near-neighbour exchange constant and S the spin. In the present case, however, the band origin at 6080 Å is extremely narrow (fig. 5). It is an electric-dipole transition, i.e. an exciton–magnon combination band, and its behaviour with respect to temperature and external magnetic fields confirm that it is correlated with the magnetic order. Specifically, it is only present when the crystal is in the incommensurate helical magnetic phase and, from its temperature dependence and polarisation, is associated with creation of magnons propagating within

the basal plane. From the arguments given above, the sharpness of the band implies that the exciton must be coupling to a very sharply peaked density of magnon states.

In their theoretical work on the stability and excitations of non-collinear magnetic structures in two-dimensional lattices of hexagonal symmetry Rastelli *et al.*[6] give the dispersion curve for magnons in a helical phase such as has been found experimentally in $NiBr_2$, and, in so doing, show how singularities in the density of magnon states might arise. To summarize their conclusions, if the in-plane anisotropy (d) and inter-plane exchange constant (j') are assumed negligible, the magnon dispersion curve [$\omega_m(k)$ against k] has a cusp and $\omega_m(k)$ becomes zero at $k = \pm Q$, where Q is the propagation vector of the helix. The physical significance of the cusp is that the incommensurately modulated magnetic phase has a 'soft' magnon mode at a wavevector corresponding to that of the helix, roughly as 'soft' phonons are associated with structurally modulated phases, like Kohn anomalies in one-dimensional metals. For small but finite anisotropy and $j' \neq 0$ the cusp is replaced by a minimum close to $k = \pm Q$ at a small but finite frequency. In that case one expects two turning points in the dispersion relation, corresponding to the maximum preceding the minimum and at the minimum itself, this giving rise to two sharp peaks in the frequency dependence of the density-of-states. We conjecture that it is these peaks which give rise to the sharp exciton–magnon combination bands A and B.

The exchange constants in $NiBr_2$ are at present being investigated by inelastic neutron scattering[9] but if we take $j_2 (= J_2/J_1)$ as -0.22 and $d = 0.0015$ from the values found in $NiCl_2$ and $j_3 (= J_3/J_1)$ as approximately -0.10 from the limiting low-temperature value of the propagation vector in $NiBr_2$,[1-3] the energy of the minimum in the magnon dispersion curve is *ca.* 5 cm^{-1} and of the maximum *ca.* 10 cm^{-1}. In fact bands A and B are 8 cm^{-1} apart, in reasonable agreement with expectation. Moreover, the fact that the two bands move towards one another with increasing temperature can also be taken as evidence that they arise from the combination of an exciton with magnons associated with the two peaks in the magnon density-of-states. The higher frequency (and weaker) combination band B must be associated with the maximum in the spin-wave dispersion, which occurs at $k \approx 0.5Q$, and the lower-frequency band A with the minimum at $k = Q$. Now we know from the neutron diffraction that Q decreases smoothly with increasing temperature so the minimum in the magnon dispersion should likewise be displaced towards the zone centre. When the commensurate phase is regained the dispersion will once again be a monotonically increasing function of k, no doubt approximating k^2 near the zone centre, as required of a two-dimensional easy-plane ferro-magnet with small anisotropy (*e.g.* $NiCl_2$).[10] Both turning points away from $k = 0$ will have disappeared.

Although no theory is available yet to explain the effect, one could readily anticipate, nevertheless, that at intermediate temperatures moving up towards the incommensurate–commensurate transition temperature the maximum in the magnon dispersion will have diminished and its energy will be lowered. Since the lower-frequency combination band remains almost constant while the frequency of the upper one moves down towards it (fig. 2), it seems safe to suggest that the minimum in the dispersion curve also remains constant as the temperature rises. According to Rastelli's theory[6] the energy of the minimum is a function of d, j' and j_2, none of which is likely to vary between 4 and 23 K, since the lattice constants are quite unchanged over this temperature range.[4]

Introducing Zn into the lattice disorders the propagation direction but only has a small effect on the propagation length of the incommensurate helical phase.[7] Also

the temperature and applied field needed to induce a transition back to the commensurate phase are both reduced slightly. In this respect the behaviour of the 6080 Å band system complements the neutron-scattering data on the magnetic phase diagram. As one can see from fig. 7 the existence region of the helical phase in the (H, T) plane, as mapped by following the disappearance of the 6080 Å band in the 8% Zn doped crystal, agrees nicely with that obtained by following the field dependence of the magnetic satellite reflections. The same figure also includes the phase diagram of a 5.5% Zn doped crystal obtained by optical means.
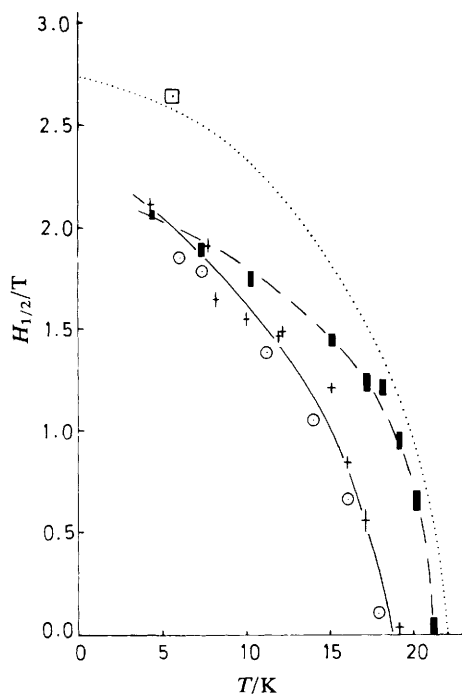

FIG. 7.—Magnetic phase diagrams. Dotted line is that of $NiBr_2$ determined optically. $Ni_{0.92}Zn_{0.08}Br_2$: circles from neutron diffraction, crosses from optical spectroscopy. $Ni_{0.945}Zn_{0.055}Br_2$, filled rectangle from optical spectroscopy.

There has been some discussion[2,6,7] as to the order of the transition from the incommensurate to the commensurate phase, both in $NiBr_2$ and its solid solutions with Zn. Adam et al.[3] suggest that in $NiBr_2$ itself the transition is first-order in temperature, although the coexistence region between the two phases is probably <1 K. On the other hand the areas of the two 6080 Å bands decrease linearly with temperature over a larger temperature interval (fig. 3). In the Zn doped compounds the question is clarified because the coexistence region is enlarged with respect both to temperature and applied field. The range of ca. 0.3 T over which the intensity of band A falls linearly to zero at 5 K quite closely parallels the field range over which the $(003)_m$ diffraction peak of the commensurate structure grows linearly with respect to the satellites.[7] Thus our results confirm that the transition is indeed first order.

CONCLUSIONS

The optical studies on $NiBr_2$ and its solid solutions with Zn complement the neutron-diffraction results. The sharp optical lines A and B in $NiBr_2$ are electric-dipole-allowed exciton–magnon combination transitions in which an exciton couples with peaks in the magnon density-of-states arising from turning points in the dispersion relations which appear as a result of the incommensurate helical spin structure. As yet there are no measurements of magnon dispersion curves for $NiBr_2$ in its helical phase which are sufficiently well-defined at the low values of energy and wavevector needed to resolve the maximum and minimum predicted by the theory of Rastelli *et al.*[6] We have argued that the optical results reported in this paper reflect the evolution of the magnon dispersion curve with temperature, in particular of the relative movement of the turning points. Unfortunately at present no theory exists to explain the temperature dependence of the propagation vector in $NiBr_2$, though since the unit-cell parameters do not vary between 4.2 and 23 K it cannot be due to any variation in the exchange constants. This conclusion is reinforced by the fact that the propagation vector is actually reduced by hydrostatic pressure.[11] One may speculate that it arises from a magnon–magnon interaction effect.

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