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RAMAN SCATTERING FROM PHONONS AND MAGNONS IN ANTIFERROMAGNETIC Fe_3BO_6

H. Navarro*, J.E. Potts† and R. Merlin

Department of Physics, University of Michigan, Ann Arbor, MI 48109, U.S.A.

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Raman scattering by phonons and by magnon pairs has been observed in Fe_3BO_6. Of the predicted 60 Raman-active modes, 39 have been identified and classified according to their symmetries. The two-magnon band shows a strong decrease in intensity with increasing temperature, and almost vanishes close to $T_N = 508$ K. The origin of this effect is attributed to the existence of a nearly dispersionless magnon branch.

Fe_3BO_6 IS A CANTED antiferromagnet ($T_N = 508$ K) [1] which crystallizes in the orthorhombic $D_{2h}^{16}(Pnma)$ structure with four formula units per unit cell [2]. The Fe spins couple ferromagnetically within (001) planes and, in successive (001) planes, they are oriented ↑↓ [3]. At $T_{SR} = 415$ K, a sudden spin reorientation takes place where the weak ferromagnetic moment rotates by 90° [3]. Depending on the temperature, the spins are almost parallel to either an equivalent [001] (for $T < T_{SR}$) or [100] direction ($T_{SR} < T < T_N$) [3].

To our knowledge, no study of the phonon spectrum of Fe_3BO_6 has been previously reported. Reference to the magnon structure is found in the optical absorption data which shows the presence of a magnon (hot) sideband 419 cm^{-1} below the $I|0, 3/2\rangle$ exciton [4]. Five optical magnon branches are expected in Fe_3BO_6. As shown below, the branch involved in the optical process gives the strongest contribution to two-magnon scattering.

The sample for this study was a single crystal, 3 × 3 × 1 mm, grown by chemical transport. Because Fe_3BO_6 is quite opaque in the visible ($\alpha \simeq 10^4$–10^5 cm^{-1}) [4], the Raman measurements were made in the backscattering geometry using the 6471 Å line of a Kr^+-laser; incident power levels were kept low ($\lesssim 50$ mW) to prevent sample heating. A Spex 1403 double monochromator and a RCA 31034A photomultiplier were used for detecting the scattered light.

Site group analysis [5] shows that the allowed Raman modes in Fe_3BO_6 transform as $17A_g + 13B_{1g} + 17B_{2g} + 13B_{3g}$. We have identified 39 of the predicted 60 active phonons and listed the room-temperature energies in Table 1. None of these modes exhibits any unusual temperature dependence of its frequency or intensity which might be correlated with the magnetic transitions. The feature that we assign to the scattering by a magnon pair occurs in the $x(zz)\bar{x}$ A_g-spectrum at 742 cm^{-1} (300 K). It is shown at temperature below and above T_N in Fig. 1, which also shows the 616 cm^{-1} A_g-phonon. Our assignment of the 742 cm^{-1}-peak as due to two-magnon scattering is based, first, on the data of Fig. 2 which shows the temperature dependence of the integrated intensity of this structure. The rapid decrease in intensity and the near disappearance at, or just above, T_N is a strong indication that the scattering involves a magnetic excitation. In addition, the value of 742 cm^{-1} is only ≈ 10% less than twice the energy of the magnon determined from the optical data [4]. It is well known that magnon-magnon interactions play an essential role in determining the structure of two-magnon spectra [5]. This is because the magnons created in the scattering process are close together in real space and, therefore, interact strongly. We attribute the 10% difference to the renormalization of magnon-pair frequencies due to this effect and, consequently, we ascribe our peak and the magnon-sideband [4] to the same magnon branch.

Further, although indirect, support for our assignment is suggested by a comparison with the case of hematite (α-Fe_2O_3) which also exhibits a two-magnon structure with intensity approaching zero in the vicinity of T_N [7]. The two-magnon band in α-Fe_2O_3 is extremely narrow ($\Gamma/\Omega \approx 0.03$ at $T = 0.08\ T_N$; Γ is the FWHM and Ω the peak position) and shifts toward lower energies by less than 2% when T goes from 0.08 T_N to 0.75 T_N [7]. As shown in Fig. 3, the corresponding values for Fe_3BO_6 are comparable: $\Gamma/\Omega \approx 0.01$ at $T = 0.2\ T_N$ and a shift of ≈ 3% in the temperature range $0.2T_N < T < 1.1T_N$. The narrow width in α-Fe_2O_3

* Permanent address: Departmento de Física. Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue-México.

† Permanent address: Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI 48128, U.S.A.

Table 1. Energies of the 39 observed optical phonons (in units of cm^{-1}*) at* T = 300 K

A_g	B_{1g}	B_{2g}	B_{3g}
124, 166	164	150, 184	114, 154, 178
204, 240, 294	218, 260	221	
320, 332, 388	382	318, 390	386
400	428, 470	418, 448	408, 456
508	592		
616		610	630
714, 742			
822		890	
986	910		

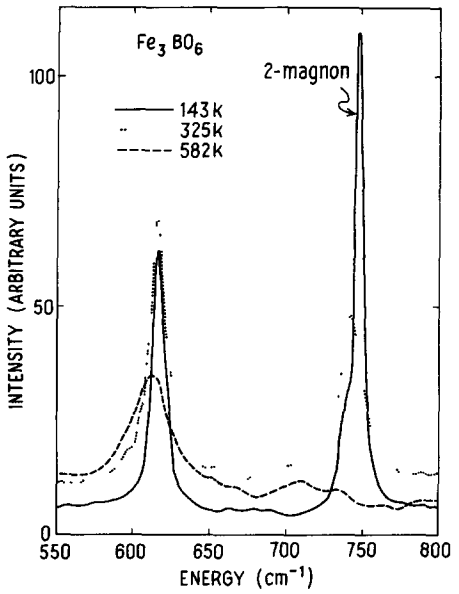

Fig. 1. Spectra of Fe_3BO_6 for different temperatures showing the two-magnon peak and the A_g-phonon at 616 cm^{-1}.

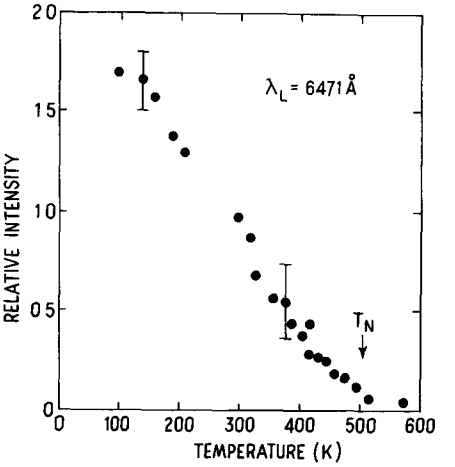

Fig. 2. Intensity of the two-magnon peak, measured relative to the intensity of the 616 cm^{-1} $-A_g$ phonon, as a function of temperature. The arrow indicates the Nèel temperature.

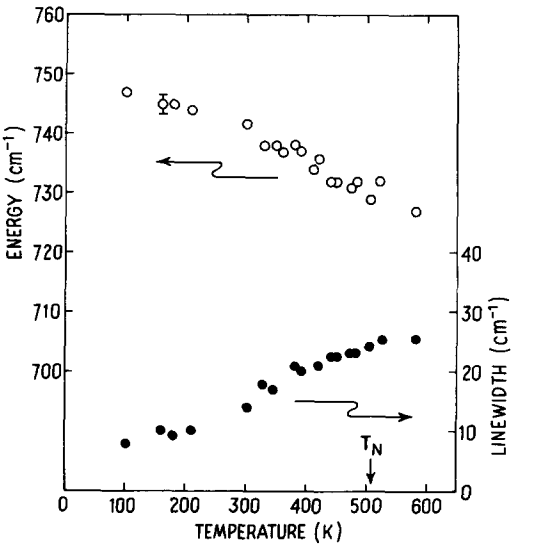

Fig. 3. Temperature dependence of the peak position (left ordinate) and the linewidth (right ordinate) of the two-magnon band. The Nèel temperature is indicated by an arrow.

originates in the nearly dispersionless optical-magnon branch [8], as determined by neutron scattering measurements [9]. Based on the similar properties of the Raman data for the two materials, we conclude that an almost dispersionless branch should also occur in Fe_3BO_6.

The Fe spins in α-Fe_2O_3 are strongly coupled to 12 nearest neighbors (nn) that belong to the opposite sublattice but only weakly coupled to a single nn with the same spin orientation [10]. Such a tightly-coupled cluster of spins leads to essentially localized excitations and, consequently, to a flat magnon branch. The source of localization in Fe_3BO_6 is not apparent as the exchange constants of this material are not yet available. A possibility is that the clusters are made out of just those two spins associated with pairs of Fe-ions 2.81 Å apart, for which the coupling to the further distant nn is likely to be substantially reduced [4].

Finally, we consider the temperature dependence of the scattering intensity in both Fe_3BO_6 and α-Fe_2O_3. There are few theoretical predictions concerning the high-temperature behavior of two-magnon spectra [11]. A calculation of four-spin static correlations at $T = \infty$ and $T = 0$ indicates that [12]

$$I_\infty/I_0 = 1/3(S+1)^2. \quad (1)$$

This prediction, valid only for two-sublattice antiferromagnets, appears to be in reasonable agreement with the few experimental results that are available [11, 12]. Clearly, equation (1) cannot be applied to our data. We believe that the diminution of the scattering strength in Fe_3BO_6 and hematite relates to the thermal break-up of the spin clusters discussed above. The misalignment of just one of the spins in a cluster leads to a shift of its lowest excitation energy out of the narrow localized band, so that it will no longer contribute to the observed peak. The Raman intensity should reflect the probability of finding a cluster with the moments properly aligned and should therefore behave, at least qualitatively, in the manner which we observe. Calculations to develop this idea for the specific cases of Fe_3BO_6 and α-Fe_2O_3 are currently underway.

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