

Effect of pressure on 2-magnon Raman scattering in K_2NiF_4

V. V. Struzhkin*, U. Schwarz, H. Wilhelm and K. Syassen

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80 (Germany)

Abstract

We measured the effect of pressure ($P \leq 10$ GPa) on 2-magnon excitations ($T = 10$ K) and on lattice parameters ($T = 300$ K) of K_2NiF_4 by Raman spectroscopy and X-ray diffraction respectively. The results allow us to determine the dependence of the superexchange interaction J on the transition metal to anion distance d . We find that J scales as $J \propto d^{-n}$ with $n = 9.5 \pm 0.5$. Previous measurements of 2-magnon excitations under pressure in NiO ($n \approx 7-8$), La_2CuO_4 and Eu_2CuO_4 ($n \approx 5-6$) are analyzed and an explanation for the trends in the pressure dependence of the superexchange interaction J is proposed.

The pressure dependence of the superexchange integral J in the antiferromagnets La_2CuO_4 and Eu_2CuO_4 [1, 2] reveals an anomalous scaling of J with cation-anion (Cu-O) distance d : $J \propto d^{-5 \pm 2}$. This behavior contradicts the empirical expression $J \propto d^{-11 \pm 1}$ [3, 4], which was derived from an analysis of previous data on the superexchange integral in various antiferromagnetic compounds. K_2NiF_4 is a prototype antiferromagnet with crystal structure analogous to La_2CuO_4 . Its Neel temperature is $T_N = 97.1$ K [5]. In K_2NiF_4 the perovskite-like layers of $KNiF_3$ are separated by planes of KF. This makes the antiferromagnetic interaction essentially two dimensional. Two-magnon Raman scattering in K_2NiF_4 is well described by the spin-wave theory [6] in the Green-function formalism for an $S = 1$ antiferromagnet. Thus, the frequency of the 2-magnon Raman line is proportional to the superexchange integral J . We measured 2-magnon Raman scattering under pressure in K_2NiF_4 in order to determine the pressure dependence of J . We also determined the pressure dependence of the lattice parameters of K_2NiF_4 using X-ray diffraction. These measurements allow us to determine the $J(d)$ dependence, which we compare with that of La_2CuO_4 [1], Eu_2CuO_4 [2] and NiO [7, 8]. We propose an explanation for the observed trends in the $J(d)$ dependences in these antiferromagnets, which is based on the theoretical model of ref. 9.

The compound K_2NiF_4 cannot be grown directly from the melt. Samples were prepared in a manner analogous to that described in ref. 10. For Raman

measurements good optical quality wafers ($100 \times 100 \times 30 \mu m^3$) were placed in a gasketed diamond-window high-pressure cell [11]. Condensed helium was used as a pressure transmitting medium in order to ensure the best possible hydrostatic conditions at low temperatures. The pressure in the cell was only changed at room temperature, and then the cell was cooled down to 10 K. Low-temperature Raman spectra were measured with a multichannel spectrometer system.

For X-ray diffraction investigations the crystals were powdered. Samples were placed in a 4:1 methanol-ethanol pressure medium. The powder pattern was observed down to a d -spacing of 1.4 Å using an angle-dispersive diffraction geometry (Debye-Scherrer method, filtered Mo $K\alpha$ radiation) and a position-sensitive proportional counter system. Experimental errors in absolute lattice parameters are estimated to be about 0.2%. The ruby luminescence method with calibration according to ref. 12 was used to measure the pressure in Raman as well as in X-ray diffraction studies.

The lattice parameters of K_2NiF_4 under normal conditions are $a_0 = 4.008(2)$ Å and $c_0 = 13.064(2)$ Å. The pressure-volume data are well fitted by a Murnaghan equation of state [13] with bulk modulus $B_0 = 56.3(25)$ GPa and its derivative $B_0' = 5.7(10)$. The pressure dependence of $d(Ni-F)$ is given by the pressure dependence of the lattice parameter a which is also well fitted by a Murnaghan-like equation $a(P) = a_0 [1 + (K_0'/K_0)P]^{-1/K_0'}$, P is the pressure in gigapascals, using $K_0 = 183(4)$ GPa, $K_0' = 18$.

Figure 1 shows 2-magnon Raman spectra of K_2NiF_4 at several pressures. The pressure dependence of the 2-magnon Raman line is shown in Fig. 2. This depen-

*On leave from: Institute for High Pressure Physics, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russian Federation.

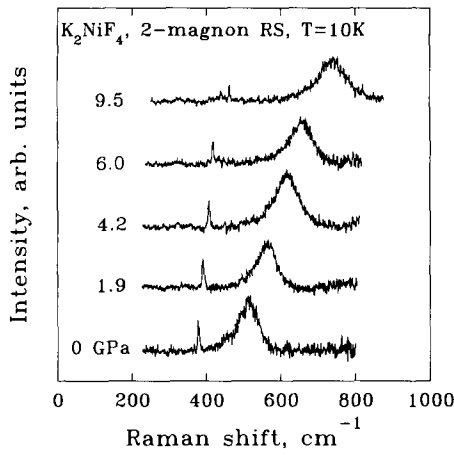


Fig. 1. Raman spectra of K_2NiF_4 ($T=10$ K) at different pressures, showing the shift of the 2-magnon Raman line.

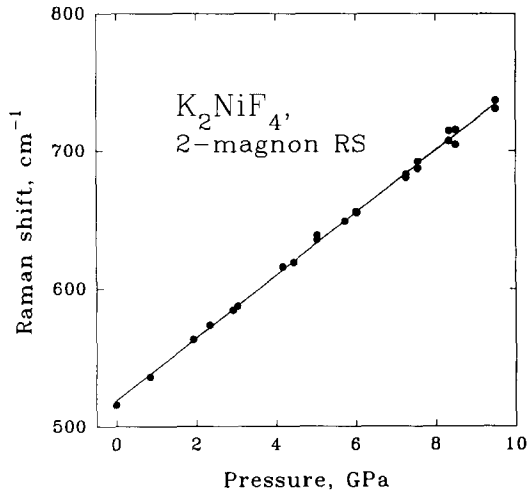


Fig. 2. Frequency of the 2-magnon Raman line in K_2NiF_4 as a function of pressure ($T=10$ K).

dence is found to be essentially linear (pressure coefficient $22.7(1.4) \text{ cm}^{-1} \text{ GPa}^{-1}$).

In order to compare previous results with ours we use the coordinates $x = \ln(d/d_0)$, $y = -\ln(J/J_0)/\ln(d/d_0)$ and show the corresponding data for K_2NiF_4 , NiO [7, 8], La_2CuO_4 [1] and Eu_2CuO_4 [2] in Fig. 3. In their interpretation of the pressure dependence of J for NiO, Massey *et al.* [8] used early compressibility data [14]. We have corrected these P - V data using Decker's [15] equation of state for NaCl, and have used corrected values of the bulk modulus of NiO ($B_0 = 170$ GPa), and its pressure derivative ($B_0' = 4$). In the case of La_2CuO_4 we have used the results of Aronson *et al.* [1] without any corrections. For Eu_2CuO_4 the situation with respect to compressibility data is most uncertain. The in-plane linear compressibility of Eu_2CuO_4 is

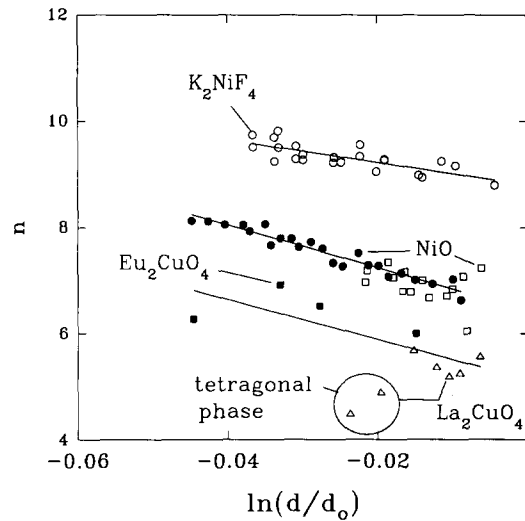


Fig. 3. Logarithmic plot of $n = -\ln(J/J_0)/\ln(d/d_0)$ vs. $\ln(d/d_0)$ for several antiferromagnets. For NiO full symbols are from ref. 8, open symbols are from ref. 7.

estimated to be $k = -1.3 \times 10^{-3} \text{ GPa}^{-1}$ based on the results for Nd_2CuO_4 [16]. Another estimate is to take the linear compressibility of the in-plane lattice parameter a for La_2CuO_4 in the orthorhombic phase [17] $k = -1.5 \times 10^{-3} \text{ GPa}^{-1}$, which is in fact quite close to the previous value. Because of this uncertainty the data for Eu_2CuO_4 are to be considered with some caution. As can be seen from Fig. 3, we cannot describe the experimental results with a single scaling law $J \propto d^{-n}$, where $n=10-12$, as was proposed earlier for the superexchange interaction [3, 4]. This even holds if we take into account the uncertainties in the compressibilities.

The pressure dependence of J can be discussed in terms of the superexchange interaction as derived from an effective Hubbard Hamiltonian [9]:

$$J = \frac{4t^4}{\Delta^2} \left(\frac{1}{U} + \frac{1}{\Delta} \right) \quad (1)$$

Δ is the charge transfer gap, U is the Mott-Hubbard gap, $t \ll \Delta$, U is the p-d matrix element. It is assumed that the Hubbard U is independent of pressure, and that t scales as $t \propto d^{-4}$.

If one places the three insulators K_2NiF_4 , NiO and La_2CuO_4 on the well known Zaanen-Sawatzky-Allen diagram [18], see Fig. 4, then La_2CuO_4 and other cuprates will be in the region of the charge-transfer insulators, for which $\Delta < U$, NiO will be close to the intermediate region $\Delta \approx U$, and K_2NiF_4 will be situated in the $\Delta > U$ region of the diagram, being a Mott-Hubbard insulator. Here we have used for La_2CuO_4 and NiO the parameter values from refs. 19 and 20. The Δ and U values for K_2NiF_4 were deter-

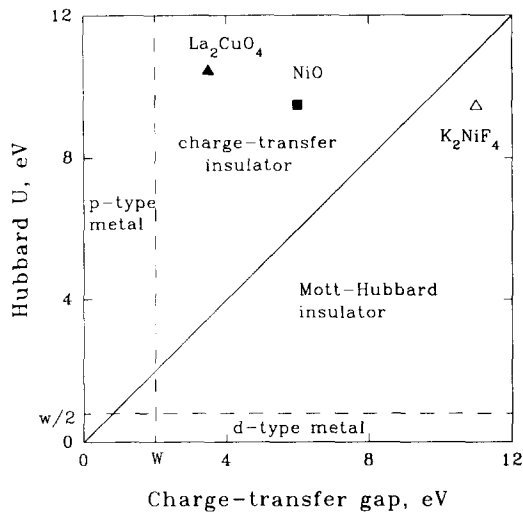


Fig. 4. Zaanen-Sawatzky-Allen diagram. The line $\Delta = U$ divides the charge-transfer insulators from Mott-Hubbard insulators. W is the p-bandwidth, w is the d-bandwidth.

mined using cation and anion systematics as given by Zaanen and Sawatzky [20, 21]. It is clear from Fig. 3 that the deviation from the empirical Bloch law $J \propto d^{-10}$ [4] correlates with the value of the charge-transfer gap, see Fig. 4. More specifically, the power n is lower for lower values of the charge-transfer gap. This correlation becomes plausible in the framework of the ionic model [22], taking into account the Madelung energies of the initial and final states of the charge-transfer transition. Quantitative treatment of Δ is not possible at present, but for model purposes we will use an approach proposed by Ohta *et al.* [23]:

$$\Delta = \Delta E_{\text{mad}} / \epsilon_{\infty} - E_1^i - E_A^i - e^2/d \quad (2)$$

ΔE_{mad} is the difference in Madelung energies at cation and anion sites, ϵ_{∞} is the dielectric constant at frequencies higher than the frequency of the charge-transfer transition, E_1^i is the ionization potential of the cation, and E_A^i is the electron affinity of the anion. The e^2/d term accounts for the Coulomb interaction of an electron and a hole, introduced by the charge-transfer transition, d is the cation-anion distance. E_1^i and E_A^i are pressure independent and we expect that the major contribution to the pressure dependence comes from the Madelung potential and the term e^2/d . Coulomb terms scale with distance as d^{-1} , but owing to the term $E_1^i + E_A^i$ in eqn. (2), which partly compensates for the Coulomb terms, the effective scaling of the charge-transfer gap is $\Delta \propto d^{-m}$, where $m > 1$. The value of m becomes larger when absolute values of the Coulomb terms and the term $E_1^i + E_A^i$ become nearly equal in magnitude, thus reducing the charge-transfer gap. This explains qualitatively the systematic variation of the J

scaling coefficient with the charge-transfer gap (see eqn. (1)). For a smaller charge-transfer gap the scaling coefficient m is larger and the resulting scaling coefficient n for J is reduced. Moreover, the scaling coefficient m of Δ also varies with d and this makes it impossible to describe the $J(d)$ dependence with the single exponent n .

Summing up, the Bloch empirical law $J \propto d^{-10}$ is approximately valid for K_2NiF_4 , but it is not valid for cuprates or for NiO. Using a perturbative expression for the superexchange interaction [19] and an ionic model [23], we find that the pressure dependence of the charge-transfer gap Δ explains the observed trends in the $J(d)$ dependence in the compounds considered here. It is worth noting that recent results on CoO [24], which has $\Delta = 7.2$ eV [20], give a $J \propto d^{-8 \pm 0.5}$ dependence. This is consistent with the interpretation given in this work, because CoO has a value of charge-transfer gap intermediate between those of NiO and K_2NiF_4 , and its scaling coefficient $n = 8 \pm 0.5$ also has an intermediate value between $n = 7.5$ for NiO and $n = 9.5$ for K_2NiF_4 .

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