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MAGNETIC EXCITATIONS IN THE CUBIC ANTIFERROMAGNET ErCu

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Résumé. — Nous avons étudié les excitations magnétiques du composé antiferromagnétique ErCu (structure cubique du type CsCl) par diffusion inélastique de neutrons à 4,3 K. Les données sont analysées à l'aide d'un modèle de susceptibilité généralisée, en tenant compte de l'Hamiltonien de champ cristallin et de l'échange bilinéaire anisotrope. Des interactions jusqu'aux quatrièmes voisins semblent suffisantes pour décrire les relations de dispersion ; l'introduction d'interactions d'ordre supérieur ou de termes magnétoélastiques améliore le calcul de la position en énergie des branches.

Abstract. — The magnetic excitations of the antiferromagnetic compound ErCu (cubic CsCl structure) have been studied by inelastic neutron scattering at 4.3 K. The data are analysed within a generalized susceptibility model, taking into account the crystal field Hamiltonian and anisotropic bilinear exchange. Interactions up to the fourth neighbours seem sufficient to describe the dispersion relations ; the addition of higher order interactions or magnetoelastic terms improves the fit of the spin wave energy gaps.

1. Introduction. — Numerous experiments have been undertaken in order to study the magnetic interactions *via* conduction electrons in rare earth intermetallics. Particularly, spin waves studies have given very precise information in pure rare earths. Such experiments, in terbium for instance [1], have shown that the Heisenberg interactions and single-ion anisotropy were the dominant terms, but that magnetoelastic couplings and two-ion anisotropy have also important effects on the energy gap and the dispersion relations.

We reported in a previous study [2] an investigation of the spin wave spectrum of the cubic ferromagnet HoZn. We describe in the following similar experiments undertaken on the isomorphous antiferromagnet ErCu.

After a description of the static properties of this compound, we give the results obtained for the spin wave spectrum. Then we analyse the data within a dynamical susceptibility model [3].

2. Magnetostatic properties and crystal field. — ErCu crystallizes with the cubic CsCl-type structure, the lattice parameter is $a = 3.430 \text{ \AA}$ at room tem-

perature. The Néel temperature is $T_N = 16 \pm 1 \text{ K}$ [4, 5]. Walline and Wallace [4] have observed a slight curvature in the variation of the reciprocal susceptibility. However, the deviation from the linearity is less than 3 K from 25 to 290 K. Fitting their points by a straight line gives a value close to our determination [5] for the Curie paramagnetic temperature. Thus θ_p is estimated to be $-14 \pm 4 \text{ K}$.

The antiferromagnetic structure is of C-type with a propagation vector $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, 0)$ [6]. The moments are aligned along the c -axis of the tetragonal magnetic cell ($a' = b' = a\sqrt{2}$, $c' = a$), assuming a collinear structure (Fig. 1).

A small magnetostriction, of the order of $1 \text{ } \mu\text{m/m}$ if tetragonal, has been detected by X-ray patterns at low temperatures [7].

The crystal field parameters have been determined previously by inelastic neutron scattering on the diluted paramagnetic compound $\text{Er}_{0.2}\text{Y}_{0.8}\text{Cu}$ [8]. Following Lea *et al.* [9], the level scheme is described by the two parameters $W = -0.64 \text{ K}$, $x = +0.34$, giving a $\Gamma_8^{(3)}$ quartet as ground state. The corresponding one-ion anisotropy favours a moment direc-

Fig. 1. — a) Magnetic structure of ErCu at 4.2 K (Ref. [6]). b) Crystallographic Brillouin zone (continuous lines) and magnetic Brillouin zone (dashed lines) for a single domain of ErCu. Γ and M' (X'' and R) are equivalent points with respect to the magnetic Brillouin zone.

tion along a quaternary axis, in agreement with the above collinear magnetic structure.

The magnetization, studied in fields up to 70 kOe [5], shows a reversible spin flopping phenomenon near 30 kOe, and the reversibility confirms the existence of magnetostrictive effects.

3. Spin wave spectrum. — The spin wave spectrum was studied on the triple axis spectrometer IN2 of the Institut Laue-Langevin at Grenoble. The sample was a $25 \times 25 \text{ mm}^2$ platelet 2 mm thick, made of two crystals cut perpendicularly to a binary axis; another binary axis was set vertically giving a (110) diffraction plane.

The spectrometer was operated in the constant q mode. The incident wave vector was $k_i = 2.662 \text{ \AA}^{-1}$, the corresponding wavelength being filtered by pyrolytic graphite. The energy transfers ranged from 0.2 to 2.4 THz.

Two branches of excitations were followed at 4.3 K along the principal symmetry directions of the crystallographic Brillouin zone (Fig. 1, 2), except for

Fig. 2. — Dispersion curves of ErCu at 4.3 K. Circles are experimental data. The curves are calculated with the parameters $W = -0.64 \text{ K}$, $x = 0.34$, $\lambda = -0.47 \text{ K}$ and $B_2 = -0.6 \text{ mK}$ and the 4 interactions J_{ij} listed in table I. Triangles refer to experimental data at 9 K.

the XM direction which could not be investigated with the sample geometry. The first branch ranges from 0.42 THz at M point to 0.67 THz at R point (20.4 K and 32.2 K respectively) the second one has a much weaker dispersion around 1.28 THz (61.5 K) and a smaller intensity. The observed intensity ratio is generally between 14 and 23 (Fig. 3); after corrections

FIG. 3. — Energy distribution of scattered neutrons for different wave vectors Q (in units of $2\pi/a$). The counting times range from 54 s to 162 s.

for the spectrometer resolution, it ranges between 9 and 15. Some points of the first branch were recorded at 9 K, showing a shift to lower energies.

As usual in cubic antiferromagnets, it is necessary to consider the different antiferromagnetic domains and the intersections of their own Brillouin zone with the diffraction plane [10]; in principle this gives rise to different dispersion curves. The effect of different domains should be more important near M, as M' is a center of a magnetic Brillouin zone and M'' is at a corner.

4. Formalism. — In this section, we first derive the complete Hamiltonian. It will be divided in two parts: a one-ion Hamiltonian $\mathcal{H}_1$, including the mean interactions described in a molecular field formalism, and the residual inter-ion part $\mathcal{H}_2$ which gives rise to the dispersion relations.

In the case of ErCu, the single-ion crystal field (CEF) parameters are expected to be close to the values determined in the dilute paramagnetic compound. A complete discussion of this problem is beyond the scope of this paper, and has been given elsewhere for isomorphous compounds [11-13].

The Heisenberg Hamiltonian is written as:

$$\mathcal{H} = + \sum_{i,j}' J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

where $\mathbf{S}$ is the total angular momentum, and $\sum'$ means a sum with $i \neq j$. The molecular field constant obtained from the Néel temperature is given, in Kelvin units, by:

$$\lambda = J(Q) = \sum_i' J_{ij} \exp(i\mathbf{Q} \cdot \mathbf{R}_{ij}) = - \frac{3 T_N}{2 S(S+1)}.$$

The corresponding exchange energy is around 27 K for a $7 \mu_B$ moment.

Contrary to the case of cubic ferromagnets, dipolar and/or pseudodipolar terms appear for antiferromagnets. For tetragonal magnetic symmetry, they may be written as :

$$\mathcal{H}_d = \sum_{i,j}' D_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j - 3 S_{iz} S_{jz}).$$

The pure magnetic dipolar interaction may be calculated from the magnetic structure and leads to a lowering of 1.8 K in energy when the moment is along the c -axis of the magnetic cell. This term contributes to the spin wave energy, even at zero wave-vector.

Nevertheless, it is possible [3] to treat these second order terms simultaneously by writing the bilinear interaction as :

$$\mathcal{H}_{ij} = J_{\parallel ij} S_{iz} S_{jz} + J_{\perp ij}(S_{ix} S_{jx} + S_{iy} S_{jy})$$

where

$$J_{\parallel} = J - 2D \quad \text{and} \quad J_{\perp} = J + D.$$

The magnetostriction may further lead to different exchange interactions between parallel or antiparallel first neighbours.

Moreover, one-ion or two-ion magneto-elastic terms appear with the onset of distortion. Higher order interactions between quadrupoles have also been shown to have a large influence on the magnetic properties of isomorphous RZn compounds [12]. A similar influence may be expected here, as for instance the same magnetostrictive behaviour is observed in TbCu (tetragonal distortion $\frac{c}{a} - 1 = 1.2\%$) and TbZn [9, 13].

It is possible to include all these terms within the molecular field formalism in order to obtain the one-ion Hamiltonian $\mathcal{H}_1$, but it is not so easy to treat them correctly in $\mathcal{H}_2$. Similarly, the separation of such terms from the dispersion curves is not straightforward, even with studies of excitations under an applied external field or as a function of temperature [1].

Thus the single-ion Hamiltonian will be reduced to the crystal field Hamiltonian, the mean bilinear interactions and the quadrupole-quadrupole terms; the inter-ion Hamiltonian will be reduced to the residual bilinear terms.

In order to treat the molecular field Hamiltonian in a similar way for the two sublattices (i.e. to have the same matrix elements), we perform a rotation of the coordinate frame for the down sublattice, for instance by an angle π around the x -axis. $\mathcal{H}_1$ is then written as :

$$\mathcal{H}_1 = \mathcal{H}_{\text{CEF}} + 2 J_{\parallel}(\mathbf{Q}) S_{zi} \langle S_z \rangle_T + B_2 O_2^0(i) \langle O_2^0 \rangle_T$$

where $\langle S_z \rangle_T$ and $\langle O_2^0 \rangle_T$ are the thermal averages of the magnetization and quadrupole momentum for one sublattice.

The behaviour of the lowest levels is shown in figure 4 with their matrix elements relative to the

FIG. 4. — Behaviour of the lowest levels of Er^{3+} ion in ErCu as a function of temperature. Dashed lines are calculated with $\lambda = -0.47$ K, $B_2 = 0$, and the continuous lines with $B_2 = -0.6$ mK. The matrix elements between the ground and excited levels are given at 4.3 K.

ground state for $\lambda = -0.47$ K, $B_2 = 0$ or -0.6 mK, $W = -0.64$ K and $x = 0.34$.

Due to the rotation of the coordinate frame for the second sublattice, $\mathcal{H}_2$ is written as :

$$\begin{aligned} \mathcal{H}_2 = \sum_{i,j \in \text{same}} J_{\parallel ij} S_{zi}(S_{zj} - 2 \langle S_z \rangle_T) \\ + \frac{1}{2} J_{\perp ij}(S_{+i} S_{-j} + S_{-i} S_{+j}) \\ + \sum_{i,j \in \text{diff}} J_{\parallel ij} S_{zi}(-S_{zj} + 2 \langle S_z \rangle_T) \\ + \frac{1}{2} J_{\perp ij}(S_{+i} S_{+j} + S_{-i} S_{-j}) \end{aligned}$$

where i and j belong to the same sublattice in the first summation and to different sublattices in the second summation.

In the following, we shall treat only the case of transverse excitations, as longitudinal excitations are expected here to occur at much higher energies, and J will be used instead of $J_{\perp}$ in this section.

The theoretical treatment follows the derivation due to Buyers *et al.* [3], except for the modification of interaction terms between different sublattices. The single site susceptibility is given by :

$$g^{\alpha\beta}(\omega) = \sum_{m,n} \frac{S_{\alpha mn} S_{\beta nm}(f_m - f_n)}{\omega - \omega_n + \omega_m}$$

where α, β equal $+$ or $-$, $S_{\alpha mn} = \langle m | S_{\alpha} | n \rangle$ and f_n is the Boltzmann factor. In our case the only non-zero components are $g^{+-}(\omega) = g^{-+}(-\omega)$ and g^{zz} . If we define two Fourier components of the exchange interactions :

$$\begin{aligned} J'(\mathbf{q}) &= \sum_{j \in \text{same}} J_{ij} e^{i\mathbf{q} \cdot \mathbf{R}_{ij}} \\ J''(\mathbf{q}) &= \sum_{j \in \text{diff}} J_{ij} e^{i\mathbf{q} \cdot \mathbf{R}_{ij}} \end{aligned}$$

we then obtain the transverse dynamical susceptibilities from the equations :

$$G^{\alpha\beta}(\mathbf{q}, \omega) = g^{\alpha\beta}(\omega) + J'(\mathbf{q}) g^{\alpha+}(\omega) G^{-\beta}(\mathbf{q}, \omega) \\ + J'(\mathbf{q}) g^{\alpha-}(\omega) G^{+\beta}(\mathbf{q}, \omega) \\ + J''(\mathbf{q}) g^{\alpha+}(\omega) G^{+\beta}(\mathbf{q}, \omega) \\ + J''(\mathbf{q}) g^{\alpha-}(\omega) G^{-\beta}(\mathbf{q}, \omega)$$

which replace equations (31) of reference [3].

The energies of the spin waves are given by the poles of these coupled Green's functions, or by the zeros of the denominator :

$$\Delta(\omega) = [1 - J'(\mathbf{q}) g^{+-}(\omega)] [1 - J'(\mathbf{q}) g^{-+}(\omega)] \\ - J''(\mathbf{q})^2 g^{+-}(\omega) g^{-+}(\omega) .$$

Starting with the matrix elements $S_{\alpha mn}$, $S_{\beta mn}$ and the given values for J_{ij} , the theoretical spin wave energies are obtained for each q -value by plotting $\Delta(\omega)$ as a function of energy. We may verify that $\omega(\mathbf{Q} - \mathbf{q}) = \omega(\mathbf{q})$ from the properties of $J'(\mathbf{q})$ and $J''(\mathbf{q})$.

5. Interpretation. — The two observed branches may be interpreted as transverse excitations from the ground state towards the first and third excited levels respectively. The smaller intensity and dispersion of the second branch is related to the corresponding smaller matrix element; the ratio of the square of matrix elements is about 20.5 in rough agreement with the observed intensity ratio.

If in $\mathcal{H}_1$ we take into account the cubic crystal field parameters and a molecular field constant $\lambda = -0.38$ K as obtained from the Néel temperature $T_N = 16$ K, the mean energies are calculated to be too low for the two branches, 19 and 46 K respectively. A much better fit may be obtained by increasing the magnitude of λ (-0.47 K) and introducing a term $B_2 = -0.6$ mK. This last term includes magnetoelastic contributions as well as quadrupole-quadrupole interactions, and it lowers the energy along the z -axis and thus increases the spin wave energy gaps.

The inter-ion interactions are obtained by a least squares fit of the experimental data for the first branch. We have tried to fit the dispersion curve by intro-

ducing 4 to 10 coupling parameters, without obtaining significant changes of the parameters and of the agreement factor :

$$R = [\sum (\omega_{\text{obs}} - \omega_{\text{calc}})^2]^{1/2} / (N_{\text{obs}} - N_{\text{var}}) ,$$

where ω_{obs} and ω_{calc} are the observed and calculated energies, N_{obs} the number of observations and N_{var} the number of variable parameters (Table I). Thus interactions up to the 4th neighbours seem sufficient to describe the dispersion curves, and were used to draw the theoretical fit on figure 2. We assumed here that exchange parameters between crystallographically-equivalent neighbours were identical.

We deduce from the preceding analysis

$$J_{\perp}(\mathbf{Q}) = -0.33 \text{ K} \quad \text{and} \quad J_{\perp}(0) = -0.07 \text{ K}$$

and we wish to compare these values to magneto-static data. From the Néel temperature we obtain $J(\mathbf{Q}) = -0.38$ K whereas we assumed a value $\lambda = J_{\parallel}(\mathbf{Q}) = -0.47$ K in the one-ion Hamiltonian.

There are some difficulties in deducing exactly the mean exchange interaction $J(0, 0, 0)$ in the paramagnetic state, as the experimental Curie temperature θ_p contains a crystal field-dependent contribution. A theoretical fit of the reciprocal susceptibility curve shows that the shift of θ_p due to crystal field effects is of the order of 8 K; thus the exchange part in θ_p is -6 ± 4 K, and $J(0, 0, 0)$ is estimated to be 0.14 ± 0.1 K.

Thus some discrepancies appear with the spin wave results. They may arise from the shortcomings of the molecular field model, the anisotropy of bilinear interactions, the magnetoelastic terms or higher order interactions which were neglected in the inter-ion Hamiltonian. For instance, taking into account the pure magnetic dipolar interaction gives the Fourier transform $D(\mathbf{Q}) = 0.02$ K, which partly explains the difference between $J_{\perp}(\mathbf{Q})$ and $J_{\parallel}(\mathbf{Q})$.

6. Conclusion. — We have also given in table I the interactions derived for the ferromagnetic compound HoZn obtained in a previous spin wave

TABLE I

Exchange parameters J_{ij} (mK) with different neighbours designed by their coordinates (l, m, n), as obtained from a fit of the data with 4 or 8 parameters. Values for HoZn are also given; negative values mean a ferromagnetic coupling.

lmn	100	110	111	200	210	211	220	221
ErCu	18.0	7.4	-22.5	-13.9				
($R = 1.28$ K)	± 5.1	± 3.3	± 1.6	± 2.4				
	20.7	1.9	-21.9	-14.5	1.0	6.1	0.3	3.3
($R = 1.18$ K)	± 7.4	± 4.3	± 1.9	± 2.9	± 2.5	± 2.7	± 2.3	± 2.5
HoZn	-79	-7	-19	5	-3	-5	-4	-1

study [2]. Again, care must again be taken relative to the occurrence of higher order interactions [12], although in this case Heisenberg exchange certainly predominates.

In rare earth intermetallic compounds, the most important coupling is expected to be the indirect exchange coupling *via* the band-electrons. In ErCu or HoZn, it is impossible to describe the interactions on the basis of the simple Ruderman-Kittel coupling *via* free s-electrons; this may be seen by computing for this model the energies of the spin waves propagating along different directions [14], or the energies of different spin configurations [5]. For instance, there is a large discrepancy between the computed and observed values of $J(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

In fact, various physical properties and band calculations [15] have shown a large density of d electrons in the conduction band, and the indirect exchange coupling must be drastically modified.

Dormann *et al.* [16] have studied the contribution of neighbours to the hyperfine field in gadolinium inter-metallic compounds. They show that a sign reversal occurs for the nearest neighbour contribution as a function of the interatomic distance between gadolinium atoms.

A similar behaviour is encountered in the present study for the interactions with first neighbours, as they change from antiferromagnetic to ferromagnetic by adding one electron in the band and by increasing the lattice parameter. Such behaviour may be accounted for by the variation of the direct overlap between the 5d electrons of first rare earth neighbours. The rather large coupling with third neighbours may occur through a kind of superexchange *via* Cu or Zn electrons.

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