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Magnetic Properties of Diamagnetic-Substituted Ytterbium Iron Garnet Explained by the Statistical Model of the Molecular Field. III. Curie Temperatures, Magnetic Susceptibilities, and Anisotropy of Si-Ca- and Ga-Substituted Ytterbium Iron Garnet

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The Curie temperatures, magnetic susceptibilities, and magnetic anisotropies of the following two crystal systems were determined: $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$, with $0 < x \leq 1.4$ and $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$, with $0 < x \leq 3.75$. Using the statistical-molecular-field model, we succeeded to explain the composition dependence of the Curie temperatures and magnetic anisotropies of the above crystals. It was found that the magnetic susceptibilities of the measured crystals tend to increase with the concentration of diamagnetic ions. This increase could be explained by combining the statistical model and assumptions of Clark and Callen, for concentrations up to $x = 2.25$ for Ga-substituted ytterbium iron garnet (YbIG) and up to $x = 1.04$ for Si-Ca-substituted YbIG.

I. INTRODUCTION

The statistical model of the molecular field¹⁻⁴ has been developed essentially for explaining the concentration dependence of the spontaneous magnetization of the multication ferrimagnetic garnets. Initially, this model was used to explain the spontaneous magnetization at temperatures near absolute zero. In the previous two papers, I and II,⁵ the statistical model was extended to interpret the spontaneous magnetization as a function of composition and temperature for a substituted three-magnetic-sublattice garnet. This paper reports the use of the statistical model to explain Curie temperatures, magnetic susceptibilities, and magnetic anisotropies and their dependence on concentration of magnetic ions in diamagnetic-substituted ytterbium iron garnet (YbIG).

II. CURIE TEMPERATURES

The Curie temperatures T_C of the crystals were determined in two ways: (i) directly, with a special device described in Ref. 6 for crystals with T_C above room temperature; (ii) indirectly, for crystals with T_C below room temperature. In the second case we chose two points: (a) the temperature at which the spontaneous magnetization vanishes; (b) the Curie-Weiss temperature, calculated by

fitting the formula $\chi = C/(T + \theta_{CW})$ to the experimental points above T_C , where C is the Curie constant and θ_{CW} is the Curie-Weiss temperature. The experimental results are presented in Fig. 1(a).

Nowik² calculated the composition dependence of the Curie temperatures of diamagnetic-substituted YIG, from the condition of existence of a solution for the σ_i -s at T_C , where $\sigma_i = 0$. Using this method, with the exchange parameters used in our approximations in I and II, the Curie temperature is given by

$$T_C = \frac{3}{5} J_{ad} \left\{ -2n_a \delta_a A_1 - n_d \delta_d B_1 \pm [(2n_a \delta_a A_1 - n_d \delta_d B_1)^2 + 0.25AB]^{0.5} \right\}, \quad (1)$$

where

$$A = \sum_{i=0}^{N_{ad}} P_{ad}(i) (N_{ad} - i) \cos^2 \phi_a(i),$$

$$B = \sum_{i=0}^{N_{da}} P_{da}(i) (N_{da} - i) \cos^2 \phi_d(i),$$

$$A_1 = \sum_{i=0}^{N_{ad}} P_{ad}(i) \cos^2 \phi_a(i),$$

$$B_1 = \sum_{i=0}^{N_{da}} P_{da}(i) \cos^2 \phi_d(i),$$

$$\delta_i = J_{ii}/J_{ij}.$$

It can be seen from (1) that in our approximation the Curie temperature is independent of J_{cc} and J_{cd} . This independence agrees with the fact that the Curie temperatures of RIG are almost independent of the rare-earth ion R . For collinear spins, Eq. (1) reduces to Eq. (4) of Nowik² for diamagnetically substituted YIG.

As shown in II, the equations of the σ_i do not work near T_C . Therefore, it can be assumed that Eq. (1) will not fit the experimental results. Using Eq. (1) with the exchange parameters of I we obtained T_C (YbIG) = 737 °K, compared to the experimental values of $T_C = 548$ °K.⁷ We found that even the relative change of T_C with composition as given by Eq. (1) does not correspond to the experimental values as shown by curves 2 of Fig. 1.

Rosencwaig³ calculated the composition dependence of the relative change of T_C assuming that garnets with different concentrations of diamagnetic ions obey a law of corresponding states. In order to calculate the variation of the Curie temperature we have to know the mean spin ion per formula unit and the magnetic energy per formula unit of the garnet. For the garnets $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$, the mean spin is given by

$$\bar{s}(x) = \frac{[2 + 3n_d(x)]2.5 + 2.5n_c(x)}{20}, \quad (3)$$

where we took $s_{Fe} = 2.5$ and the net spin per 3Yb^{3+}

= 2.5. The magnetic energy is composed of two terms: (i) the interaction energy between the iron ions, which is given by

$$V_{ad}(x) = J_{ad}s_{Fe}^2 \left(\sum_{m=0}^{N_{ad}} P_{ad}(m) [(N_{ad} - m) \cos \phi_a(m) - 0.5N_{aa}\delta_a \cos 2\phi_a(m)] - 1.5n_d(x)\delta_d N_{ad} \right); \quad (4)$$

(ii) the interaction energy between the Yb^{3+} ion and the iron ions, which is given by

$$V_{cd}(x) = 3n_c(x)s_{Yb} \sum_{m=0}^{N_{cd}} P_{cd}(m) [(N_{cd} - m)J_{cd} \cos \phi_c(m)s_{Fe} - 0.5N_{cc}J_{cc} \cos 2\phi_c(m)s_{Yb}]. \quad (5)$$

For the garnets $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$, the mean spin is given by

$$\bar{s}(x) = \frac{2.5[2n_a(x) + 3n_d(x)] + 2.5}{20}. \quad (6)$$

The first term of the interaction energy depends on which site canting occurs. For canting in the (d) site, we have

$$V_{ad}(x) = J_{ad}s_{Fe}^2 \left(3n_d(x) \sum_{m=0}^{N_{da}} P_{da}(m) [(N_{da} - m) \cos \phi_d(m) - 0.5N_{da}\delta_d \cos 2\phi_d(m)] - n_d(x)\delta_a N_{da} \right), \quad (7)$$

while for canting in the $[a]$ site, we have

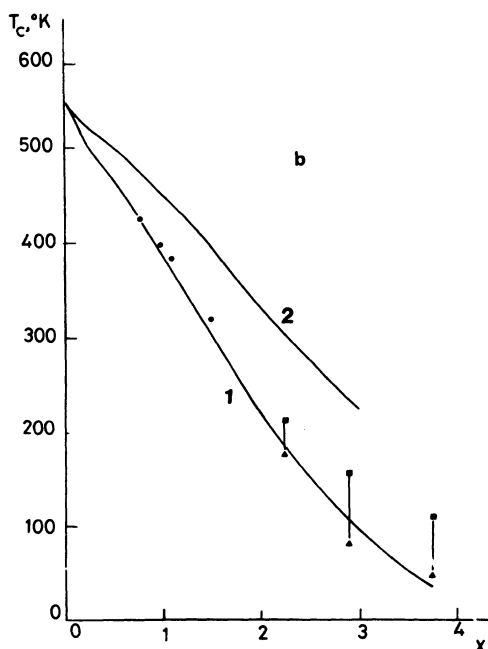
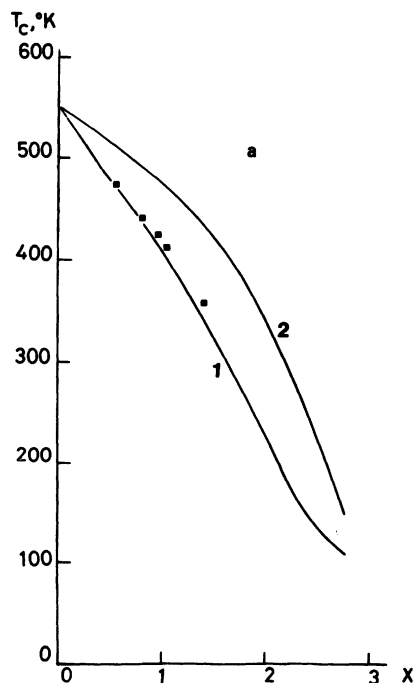


FIG. 1. Curie temperatures of diamagnetic-substituted YbIG: curves 1, calculated according to Rosencwaig (Ref. 3); curves 2, calculated according to Eq. (2). (a) Ca-Si-substituted YbIG; (b) Ga-substituted YbIG. Experimental points: ■ in (a) and ● in (b) measured; ■ in (b) from zero spontaneous magnetization; ▲, Curie-Weiss points.

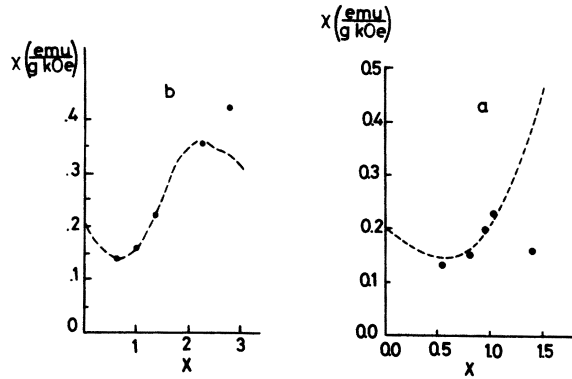


FIG. 2. Magnetic susceptibility at 4.2°K, along the [111] direction of: (a) $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$; (b) $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$. Curves, calculated; points, experimental.

$$V_{ad}(x) = J_{ad} S_{Fe}^2 \left(2n(x) \sum_{m=0}^{N_{ad}} P_{ad}(m) [(N_{ad} - m) \cos \phi_a(m) - 0.5 N_{aa} \delta_a \cos 2\phi_a(m)] - 1.5 n_d(x) \delta_d N_{dd} \right). \quad (8)$$

The second term of the energy is given in both cases above by

$$V_{cd}(x) = 3 S_{Yb} \sum_{m=0}^{N_{cd}} P_{cd}(m) [(N_{cd} - m) \cos \phi_c(m) J_{cd} S_{Fe} - 0.5 N_{cc} \cos 2\phi_c(m) J_{cc} S_{Yb}]. \quad (9)$$

For both garnet systems the total energy is given by

$$V(x) = V_{ad}(x) + V_{cd}(x). \quad (10)$$

Using Eqs. (3), (6), (10), and (23) of Rosenzweig,³ we calculated the composition dependence of the Curie temperatures and the results are plotted as curves 1 of Fig. 1. It can be seen from these figures that there is reasonable agreement between the calculated curves 1 and the experimental results.

Although it appears from the equations above that the Curie temperature depends also on the rare earth, the term V_{cd} is much smaller than the term V_{ad} . For example, $V_{cd} = 0.02 V_{ad}$ for $x = 0$ and $V_{cd} = 0.06 V_{ad}$ for $x = 3.75$ in $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$.

III. MAGNETIC SUSCEPTIBILITY

It was mentioned in Papers I and II that the magnetic moment M is linear with the magnetic field H at any temperature, for all crystals investigated. The magnetic susceptibility, defined as $(\delta M / \delta H) | T$, is therefore constant with the field. Clark and Callen⁸ found that χ of YbIG is constant up to 139 kOe. The magnetic susceptibilities at 4.2°K of all crystals investigated are presented in Fig. 2. It can be seen from Fig. 2 that from a certain concentration of diamagnetic ions the magnetic susceptibility at

4.2°K increases with increasing diamagnetic concentration.

The susceptibility increases from $x = 0.78$ for Ga-substituted YbIG and from $x = 0.55$ to $x = 1.035$ in Si-Ca-substituted YIG. Geller *et al.*⁹ found a similar phenomenon in diamagnetic-substituted YIG and attributed this increase of susceptibility to the increase in anisotropy of the garnets with diamagnetic substitution. We shall see later that in our garnets the anisotropy decreases with increasing x ; therefore the anisotropy cannot explain the increase of susceptibility. Moreover, Geller found the increase of susceptibility only for much higher diamagnetic substitutions. Clark and Callen⁸ showed that for a collinear two-sublattice ferrimagnet there is a range of fields and temperatures in which a canted configuration of the two sites exists. In this region the magnetic susceptibility of the ferrimagnet is field independent. The YbIG can be considered a two-site ferrimagnet where the magnetization of one site is $M_d - M_a$ and the magnetization of the second site is M_c , where M_i is the magnetization of site i of the garnet. Due to the fact that for YbIG at low temperatures $|M_d - M_a| \approx |M_c|$, the canted regions begin at very low fields.⁸ The susceptibility of YbIG in the canted region is given by⁸

$$\chi^{-1} = \lambda_{\text{eff}} = |(\lambda_{cd} M_d - \lambda_{ca} M_a)(M_d - M_a)|, \quad (11)$$

where λ_{ij} is the parameter of the molecular field.

Using the assumption of the random distribution of the substituted ions, the values of M_a and M_d are changing from place to place in the crystal. One needs therefore to consider the local moments m_a and m_d . The local susceptibility around a $\{c\}$ ion is variable and the measured susceptibility is the mean value of the local susceptibilities.

We shall now consider the two cases of Ca-Si- and Ga-substituted YbIG. As shown in paper I, $\lambda_{ca} = 0$ in our approximation. The local effective molecular-field coefficient of $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$ is given by

$$\lambda_{\text{eff}}(i, j) = \left| \frac{J_{cd} m_d(i)}{m_d(i) - m_a(j)} \right|, \quad (12)$$

where

$$m_d(i) = g S_d \sigma_d (\pi_{cd} - i)$$

and

$$m_a(j) = g S_a \sigma_a (N_{ca} - j), \quad (13)$$

where g is the Landé factor of the iron ions and i and j are the number of diamagnetic ions in sites $\{d\}$ and $\{a\}$, respectively. The other symbols are defined in I. The product $s_i \sigma_i$ gives the mean value of spin i in the direction of the magnetization. We took as the number of $\{d\}$ neighbors of ion $\{c\}$, $\pi_{cd} = 6$, in order to get for pure YbIG in formula (12), $M_d = 15 \mu_B$. The susceptibility of the garnet

$\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$ is given by

$$\chi = \sum_{i=1}^{\mathcal{N}_{cd}} \sum_{j=1}^{\mathcal{N}_{ca}} \mathcal{P}_{cd}(i) P_{ca}(j) \lambda_{eff}^{-1}(i, j). \quad (14)$$

$\mathcal{P}_{cd}(i)$ is calculated from Eq. (4) in I with $\mathcal{N}_{cd} = 6$.

In $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$ the number of magnetic ions in $[a]$ is constant:

$$\lambda_{eff}(i) = |J_{cd} m_d(i) [m_a(i) - m_a]^{-1}|, \quad (15)$$

with $m_d(i)$ defined by (14) and $m_a = g S_a \sigma_a N_{ca}$. The susceptibility of the garnet is given by

$$\chi = \sum_{i=1}^{\mathcal{N}_{cd}} \mathcal{P}_{cd}(i) \lambda_{eff}^{-1}(i). \quad (16)$$

The curves calculated with (15) and (16) are shown in Fig. 2. It can be seen from this figure that we get good agreement with experiment for values of x up to $x = 2.25$ in $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$ and up to $x = 1.04$ in $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$.

The above equations for χ were deduced assuming collinearity of the spins in sites $[a]$ and $[d]$ as it occurs in pure YbIG. It was shown in papers I and II that the spins in substituted garnet are no longer collinear, but form canting angles with the directions of the external magnetic field. For small values of x , the canting angles of the spins $[a]$ and $[d]$ which contribute to the total magnetization are small and one can still assume collinearity of spins $[a]$ and $[d]$ making it possible to use the assumptions of Clark and Callen⁶ and the above equations. For higher values of x there is a distribution of significant canting angles and therefore it is not possible to assume collinearity of spins $[a]$ and $[d]$. This explains the discrepancy between the calculated curves and the experimental results at high values of x .

IV. MAGNETIC ANISOTROPY

In Papers I and II the spontaneous magnetization M_0 in the easy direction $[111]$ was discussed. The

spontaneous magnetization along other crystallographic directions, like $[110]$ or $[100]$, was also determined for all crystals at 4.2°K . The ratios $r_1 = M_0[100]/M_0[111]$ and $r_2 = M_0[110]/M_0[111]$ were calculated ($M_0[hkl]$ is the spontaneous magnetization along the crystallographic direction $[hkl]$) and the results are presented in Fig. 3.

The garnet YbIG is highly anisotropic¹⁰ with the $[111]$ direction being the easy axis of magnetization. At zero external field, the spins are oriented along the $[111]$ direction. If one measures, at low temperatures, the magnetization along any crystallographic direction $[hkl]$ and extrapolates to zero external field one should obtain $r = M_0[hkl]/M_0[111] = \cos\psi$, where $M_0[hkl]$ is the spontaneous magnetization along the direction $[hkl]$ and ψ is the angle between the direction $[hkl]$ and the direction $[111]$.

We found that in all measured crystals the $[111]$ direction is the easy axis of magnetization. From the values of $\cos\psi$, we should have for all x , $r_1 = M_0[100]/M_0[111] = 3^{-1/2}$ and $r_2 = M_0[110]/M_0[111] = (2/3)^{-1/2}$.

We can see from Fig. 3 that the above relations do not apply, but instead the two ratios r_1 and r_2 increase with x . The ratios r_i are obtained assuming that the spins are strongly connected to the $[111]$ direction and that an external field only bends them slowly from this direction. In order to explain the experimental results, one has to assume that some of the spins are weakly connected to the $[111]$ direction and follow the direction of the external field from the smallest field we used (2.5 kOe). This can occur if the local anisotropy field is smaller than the external magnetic field. The anisotropy of the exchange field is a result of the interaction of the Yb^{3+} ions with the iron ions of site $[d]$ because in our approximation the ion $\{c\}$ interacts mainly with the nearest two neighbors (d) .

One can assume that a Yb^{3+} ion without a magnet-

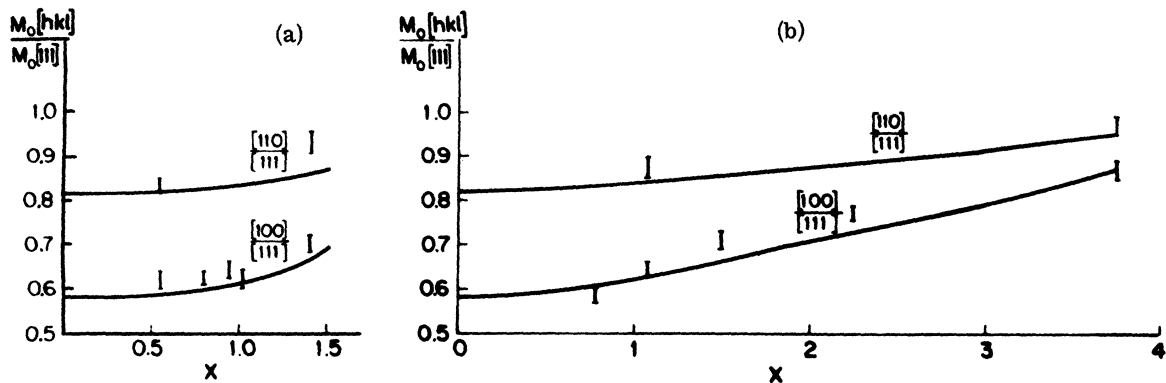


FIG. 3. Magnetic anisotropy at 4.2°K of (a) $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$; (b) $\text{Yb}_3\text{Ga}_x\text{Fe}_5\text{O}_{12}$. Curves, calculated; I, experimental

ic nearest neighbor (d) does not contribute to the anisotropy of the garnet. A fraction of the magnetic spins, proportional to the Yb^{3+} ions without any magnetic nearest neighbor (d), has low anisotropy and they follow the direction of the external field. The other spins remain connected to the $[111]$ direction. For the garnets $\text{Yb}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$, we therefore can write

$$M_0[hkl]/M_0[111] = [P_{cd}(2) + P_{cd}(1)] \cos\psi + P_{cd}(0). \quad (17)$$

For the garnets $\text{Yb}_{2.9-x}\text{Bi}_{0.1}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$, we can write

$$\frac{M_0[hkl]}{M_0[111]} = \frac{[P_{cd}(2) + P_{cd}(1)] \cos\psi n_c(x) + P_{cd}(0)[1 - n_c(x)]}{[P_{cd}(2) + P_{cd}(1)] n_c(x) + P_{cd}(0)[1 - n_c(x)]}. \quad (18)$$

The denominator in (18) is necessary for the normalization: $M_0[111]/M_0[111] = 1$. Using the relations (17) and (18) we could calculate the compositional variation of the magnetization anisotropy of the diamagnetic-substituted YbIG. The results are shown

in Fig. 3 and one can see that we obtained a fair agreement with the experimental results.

V. CONCLUSIONS

The statistical model of the molecular field with the assumptions of a distribution of canting angles proved to be a useful tool for explaining the magnetic properties of diamagnetic-substituted-YbIG systems. The statistical model was extended from the two-sublattice ferrimagnet to a three-sublattice ferrimagnet. Once the exchange parameters of pure YbIG were determined, the temperature and composition dependence of the spontaneous magnetization as well as the composition dependence of the Curie temperatures, of the magnetic anisotropies, and of the magnetic susceptibility were successfully explained.

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Temperature Dependence of Magnon-Phonon Sidebands in KMnF_3 [†]

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Temperature dependence of the fine structure in the optical-absorption spectrum is measured on the ${}^6\text{A}_1 \rightarrow [{}^4\text{E}, {}^4\text{A}_1]$ transition in KMnF_3 . All the components are classified into an excitonic transition and magnon-phonon sidebands. Some of the sidebands have the same temperature dependence as the sublattice magnetization, while the others show weak dependence with temperature. A hot band due to the magnon-phonon absorption is also observed.

I. INTRODUCTION

Optical-absorption spectra of antiferromagnetic KMnF_3 crystal exhibit complicated fine structure at low temperatures. The most interesting feature of the fine structure is that an exciton-magnon absorption mechanism is responsible for the transitions between Stark levels of the divalent manganese ion. Magnon sidebands have been observed by several workers in the first excitation band $\{ {}^6\text{A}_1(\text{S}) - {}^4\text{T}_1(\text{G}) \}^1$ and the third excitation band $\{ - [{}^4\text{A}_1(\text{G}), {}^4\text{E}(\text{G})] \}^{2-5}$. There is no ambiguity in the

assignment of excitonic transitions and magnon sidebands, although the observed magnon energies are slightly different from each other. Pickart *et al.*⁶ obtained the spin-wave dispersion relation of antiferromagnetic KMnF_3 by means of neutron inelastic scattering and compared it with theory, assuming that the antiferromagnet has a collinear magnetic structure with two interlocking face-centered-cubic sublattices. The most probable values⁶ for the nearest- and next-nearest-neighbor exchange constants and an anisotropy field lead to the following magnon energies at the critical points of