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Nuclear-quadrupole-resonance line shapes for spin 1 and the incommensurate structure of the 20*r* polytype of $K_3Co(CN)_6$ at low temperature

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The nuclear quadrupole resonance (NQR) line shape for nuclei with spin $I=1$ in incommensurate systems is obtained explicitly in terms of the changes produced in the electric field gradient by the displacement wave. We found that generally the ν^+ lines have a different shape from that of the ν^- lines in the incommensurate phase and that one obtains direct information about the changes introduced in the electric-field-gradient tensor from the NQR line shape in the plane-wave limit. A line-shape study of the ^{14}N spectrum observed in the low-temperature phase of the 20*r* polytype of $K_3Co(CN)_6$ showed incommensuration in only one N site. The measurement of the temperature dependence of the complete spectrum of the 20*r* polytype from room temperature to 77 K showed that the transition was first order and could be interpreted as resulting from the softening of a translational mode that involves the complex ion.

INTRODUCTION

Nuclear quadrupole resonance (NQR) provides information about the electric-field gradient (EFG) present at certain crystal sites occupied by nuclei with finite electric quadrupole moment.[1] Such technique has been extensively applied to the study of different types of phase transitions[2–4] as it provides detailed information about the changes produced in the interatomic distances. In particular, several commensurate-incommensurate (*C-IC*) transitions have been studied by means of NQR of halogens[5–9] with spin $\frac{3}{2}$. Only two studies were performed by means of pure ^{14}N NQR[10,11] even if such nucleus had a spin of 1 and its NQR spectrum consisted of two lines per independent site.[1] Consequently, the ^{14}N spectrum provides information about two components of the EFG tensor directly from polycrystalline samples.[1] Instead, in halogen NQR with nuclear spin $I=\frac{3}{2}$, only one frequency is obtained per site[1] so a more limited information is available from polycrystalline samples containing such nuclei. The advantage of having two lines per each site is particularly useful in the study of *C-IC* phase transitions as it provides more information about the effects of the displacement field on the EFG. On the other hand, the line shape of the quadrupole perturbed NMR lines[4,12] in *IC* phases has been analyzed from an expansion of the frequency directly in terms of the powers of the displacement field. The relationship between the NMR frequencies and the EFG tensor is complicated as the lineshape expression involves several components of that tensor.[13] Thus, it is quite difficult to separate the effects of the *IC* modulation on the different components of the EFG tensor unless one determines the complicated angular dependence of the lines in a single crystal of adequate size. However, there is a direct and simple relationship between the NQR frequencies of a nuclei with spin $I=1$ and the principal components of the EFG,[14] so one could easily obtain expressions linking the NQR line shape and the changes in the EFG produced by the *IC* wave. In this work, we have obtained those expressions in terms of the *IC* displacements[15] within the local,[12] nonlocal[16] and plane-wave approximation[4] (PWA) for nuclei with spin $I=1$. We found that the shape of the lines forming the NQR spectrum for such nuclei must be different except when the *IC* modulation only affects the EFG component along the principal *z* axis.

We have also determined the temperature dependence of the missing[17] low-frequency doublet and completed that of the other N NQR lines in the single-layer (1*M*) and in the double-layer orthorhombic (20*r*) polytypes of $K_3Co(CN)_6$ (KCO). We found that the transition observed[17] at 84 K in the 20*r* polytype was first order. We determined that the low-temperature phase of that polytype is incommensurate below T_c and that only one of the N sites is affected by the *IC* modulation. We also observed, as predicted, that the shape of the low-frequency line was different from that of the high-frequency line forming the spectrum of the *N* site affected by the *IC* modulation. From the temperature dependence of the N NQR spectrum in the *IC* phase, we determined the dependence of the first terms of the expansion of the EFG in terms of the displacements. We also discussed the details of the phase transition observed in KCO in terms of the softening of a translational mode[18] and the presence of disorder in terms of the theory of the order-disorder (OD) structures.[19,20]

EXPERIMENT

KCO was prepared according to the method described in the literature.[21] A Matec-Nicolet Fourier-transform pulse spectrometer was used in the detection of the ^{14}N lines[22] and the cryostat was similar to that used in Ref. 23. The free-induction decays were transformed with a program that provided the power spectrum. The comparison of the NQR spectrum with that of Ref. 17 showed that the samples used contained approximately the same amount of the 1*M* and 20*r* polytypes of KCO.

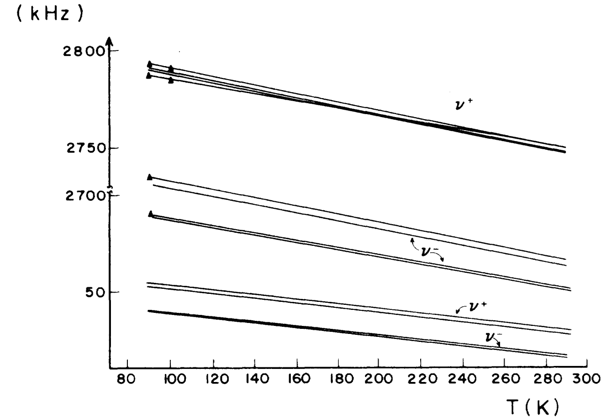

FIG. 1. Temperature dependence of the ^{14}N NQR spectrum from 84 K up to room temperature for the $1M$ and $20r$ polytypes of $K_3Co(CN)_6$. The triangles represent the frequencies obtained in Ref. 17 for the $1M$ polytype. The low-frequency doublet corresponding to the $20r$ polytype disappeared below 84 K.

RESULTS

Since ^{14}N has spin $I=1$, two NQR lines $(\nu^+ > \nu^-)$ are usually observed for each crystallographically independent N site.[1] The lines are $\nu^{\pm}=(3e^2qQ/4h)(1\pm\eta/3)$, where e^2qQ/h is the nuclear quadrupole coupling constant[1] and η is the symmetry parameter of the EFG. The complete temperature dependence of the lines for both polytypes of KCO are shown in Fig. 1. The missing low-frequency doublets[17] were found to be weaker and broader than all the other lines of both polytypes unless the samples were recrystallized several times. The temperature dependence of all the $20r$ lines was linear down to T_c and those of the $1M$ polytype showed the same behavior down to the lowest temperature achieved in this work (77 K). Below 84 K, one of the ν^+ lines of the $20r$ polytype broadened and showed a shape similar to that found in some *IC* phases[4] (see Fig. 2) while its low-frequency doublet disappeared below T_c. Repeated attempts to detect the doublet at 77 K failed even after using long accumulation times that gave excellent signal to noise ratios for all the other lines. The frequency of the reported lines[17] were in very good agreement in the range in which they overlapped with those measured in this work.

THEORY

For spin $I=1$, the ν^+ and ν^- lines are related to the principal components of the EFG as[14]

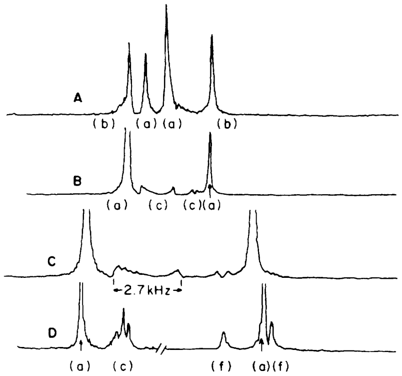

FIG. 2. ^{14}N NQR spectra of $K_3Co(CN)_6$ obtained at different temperatures. Line *A* shows the ν^+ lines of the $1M$, (a), and $20r$, (b), polytypes at room temperature; typical linewidth is around 200 Hz. In line *B*, we show the same lines at 77 K. One of the $20r$ lines, (c), showed two-edge singularities observed in other incommensurate compounds while the other $20r$ lines, (d), exhibited normal line shapes below 84 K. Line *C* is an expanded view of line *B* showing details of the incommensurate line (linewidth $\sim$2.7 kHz) together with the other narrow lines of the transformed $20r$ and the unperturbed $1M$ polytype at 77 K. Line *D* shows the five ν^- lines, (e) and (f), observed at 77 K corresponding to the transformed $20r$ polytype and the ν^- lines, (g), corresponding to the $1M$ polytype. The (f) lines have been identified as edge singularities of a single ν^- line (see text).

$$\nu^+=(V_{zz}-V_{yy})/2 , \tag{1}$$

$$\nu^-=V_{zz}+V_{yy}/2 . \tag{2}$$

where $V_{n,m}=\partial^2V/\partial x_n\partial x_m$ are the components of the EFG tensor and V is the electrostatic potential at the nuclear site. Equations similar to (1) and (2) may be obtained also for the pair V_{zz} and V_{xx}. We may write the variations in $V_{n,m}$ produced by the *IC* modulation at the position of the ith nucleus in the lth commensurate unit cell in the nonlocal approximation as[16]

$$V_{n,m}(\mathbf{x}_i)=V_{n,m}^{(0)}(\mathbf{x}_i)+\sum_j \nabla_j V_{n,m}(\mathbf{x}_i)u_j + \sum_{j,j'} u_j\nabla_{j'}[\nabla_j V_{n,m}(\mathbf{x}_i)]u_j+\cdots , \tag{3}$$

where V is the EFG in the commensurate phase and ∇_j is the field-gradient operator $\partial/\partial r_j$. We will omit from now on the index i that counts the site of the observed nuclei. More detailed information may be obtained by using Kind's definition[24] for the real displacement u_j as an admixture of symmetric (s) and antisymmetric (c) components in Eq. (3). We obtain

$$V_{n,m}=V_{n,m}^{(0)}+V_{n,m}^{(1c)}\cos[\Phi(\mathbf{x})]+V_{n,m}^{(1s)}\sin[\Phi(\mathbf{x})]+\tfrac{1}{2}\{V_{n,m}^{(2)}+V_{n,m}^{(2c)}\cos[2\Phi(\mathbf{x})]+V_{n,m}^{(2s)}\sin[2\Phi(\mathbf{x})]\}+\cdots , \tag{4}$$

where

$$V_{n,m}^{(1c)}=\sum_j \mathbf{u}^c(i,j)\nabla_j V_{n,m}^{(0)}, \quad V_{n,m}^{(1s)}=\sum_j \mathbf{u}^s(i,j)\nabla_j V_{n,m}^{(0)} ,$$

$$V_{n,m}^{(2)}=\sum_{j,j'}\mathbf{u}^c(i,j')\nabla_{j'}(\nabla_j V_{n,m}^{(0)})\mathbf{u}^s(i,j)\ ,$$

$$V_{n,m}^{(2s)}=\frac{1}{2}\left[\sum_{j,j'}\mathbf{u}^c(i,j')\nabla_{j'}(\nabla_j V_{n,m}^{(0)})\mathbf{u}^c(i,j)+\sum_{j,j'}\mathbf{u}^s(i,j')\nabla_{j'}(\nabla_j V_{n,m}^{(0)})\mathbf{u}^s(i,j)\right]\ ,$$

$$V_{n,m}^{(2c)}=\frac{1}{2}\left[\sum_{j,j'}\mathbf{u}^c(i,j')\nabla_{j'}(\nabla_j V_{n,m}^{(0)})\mathbf{u}^c(i,j)-\sum_{j,j'}\mathbf{u}^s(i,j')\nabla_{j'}(\nabla_j V_{n,m}^{(0)})\mathbf{u}^s(i,j)\right]\ ,$$

while

$$\mathbf{u}^c(i,j)=\mathbf{u}_0^c\cos[\Phi(x_j-x_i)]+\mathbf{u}_0^s\sin[\Phi(x_j-x_i)]$$

and

$$\mathbf{u}^s(i,j)=\mathbf{u}_0^s\cos[\Phi(x_j-x_i)]-\mathbf{u}_0^c\sin[\Phi(x_j-x_i)]\ .$$

We may write Eq. (4) as

$$V_{n,m}(x)=V_{n,m}^{(0)}+\Delta V_{n,m}^{(0)}$$

and obtain $\Delta V_{zz}^{(0)}$ and $\Delta V_{yy}^{(0)}$ (or $\Delta V_{xx}^{(0)}$) directly from the lineshapes of the NQR spectrum. However, we may obtain more detailed information about the changes in the EFG if we eliminate the sine terms of Eq. (4) by means of adequate phase shifts.[16] We have then

$$V_{n,m}(\mathbf{x})=V_{n,m}^{(0)}(\mathbf{x})+V_{n,m}^{(1')}\cos[\Phi(\mathbf{x})-\Phi_{1,(n,m)}]+\tfrac{1}{2}V_{n,m}^{(2')}+V_{n,m}^{(2'')}\cos\{2[\Phi(\mathbf{x})-\Phi_{2,(n,m)}]\}+\cdots\ , \tag{5}$$

where now

$$V_{n,m}^{(1')}=[(V_{n,m}^{(1c)})^2+(V_{n,m}^{(1s)})^2]^{1/2},\quad \tan\Phi_{1,(n,m)}=V_{n,m}^{(1s)}/V_{n,m}^{(1c)}\ ,$$

$$V_{n,m}^{(2')}=V_{n,m}^{(2)},\quad V_{n,m}^{(2'')}=[(V_{n,m}^{(2c)})^2+(V_{n,m}^{(2s)})^2]^{1/2},\quad \tan 2\Phi_{2,(n,m)}=V_{n,m}^{(2s)}/V_{n,m}^{(2c)}\ .$$

From Eqs. (1), (2), and (5) we have for ν^+

$$\begin{aligned}\nu^+=\nu_0^+ &+A_1^c\cos[\Phi^+(\mathbf{x})-\Phi_{1,(n,m)}]+A_1^s\sin[\Phi^+(\mathbf{x})-\Phi_{1,(n,m)}^+]+(B_2/2)\\ &+(B_2^c/2)\cos\{2[\Phi^+(\mathbf{x})-\Phi_2^+,(n,m)]\}+(B_2/2)\sin\{2[\Phi^+(\mathbf{x})-\Phi_{2,(n,m)}^+]\}+\cdots\ ,\end{aligned} \tag{6}$$

where

$$A_1^c=(V_{zz}^{(1c)}-V_{yy}^{(1c)}/2,\quad A_1^s=(V_{zz}^{(1s)}-V_{yy}^{(1s)})/2\ ,$$

$$B_2=(V_{zz}^{(2')}-V_{yy}^{(2')})/2,\quad B_2^c=(V_{zz}^{(2c)}-V_{yy}^{(2c)})/2\ ,$$

and

$$B_2^s=(V_{zz}^{(2s)}-V_{yy}^{(2s)})/2\ .$$

For ν^-, we have, instead,

$$\begin{aligned}\nu^-=\nu_0^- &+C_1^c\cos[\Phi^-(\mathbf{x})-\Phi_{1,(n,m)}^-]+C_1^s\sin[\Phi^-(\mathbf{x})-\Phi_{1,(n,m)}^-]+(D_2/2)\\ &+(D_2^c/2)\cos\{2[\Phi^-(\mathbf{x})-\Phi_{2,(n,m)}^-]\}+(D_2^s/2)\sin\{2[\Phi^-(\mathbf{x})-\Phi_{2,(n,m)}^-]\}+\cdots\ ,\end{aligned} \tag{7}$$

where

$$C_1^c=V_{zz}^{(1c)}+(V_{yy}^{(1c)}/2),\quad C_1^s=V_{zz}^{(1s)}+(V_{yy}^{(1s)}/2)\ ,$$

$$D_2=V_{zz}^{(2')}+(V_{yy}^{(2')}/2),\quad D_2^c=V_{zz}^{(2c)}+(V_{yy}^{(2c)}/2)\ ,$$

and

$$D_2^s=V_{zz}^{(2s)}+(V_{yy}^{(2s)}/2)\ .$$

We may obtain from Eqs. (5) and (6) an expression similar to that found in the local approximation[12] if we introduce phase shifts[16] as in Eq. (4). We have then

$$\nu^+=\nu_0^++\nu_1^+\cos[\Psi_+(\mathbf{x})+\overline{\Phi}_+]+\nu_2'^{+}+\nu_2^+\cos^2[\Psi_+(\mathbf{x})]+\cdots\ , \tag{8}$$

$$\nu^-=\nu_0^-+\nu_1^-\cos[\Psi_-(\mathbf{x})+\overline{\Phi}_-]+\nu_2'^{-}+\nu_2^-\cos^2[\Psi_-(\mathbf{x})]+\cdots\ , \tag{9}$$

with

$$\nu_1^+=[(A_1^c)^2+(A_1^s)^2]^{1/2},\ \ \tan\Phi_1^+=A_1^s/A_1^c,\ \ \nu_1'^+=(B_2-\nu_2^+)/2,\ \ \nu_2^+=[(B_2^c)^2+(B_2^s)^2]^{1/2}\ ,$$

$$\tan 2\Phi_2^+=B_s^2/B_2^c,\ \ \nu_1^-=[(C_1^c)^2+(C_1^s)^2]^{1/2},\ \ \tan\Phi_1^-=C_1^s/C_1^c,\ \ \nu_2'^+=(D_2-\nu_2^-)/2\ ,$$

$$\nu_2^-=[(D_2^c)^2+(D_2^s)^2]^{1/2},\ \ \tan 2\Phi_2^-=D_2^s/D_2^c,\ \ \Psi_\pm(\mathbf{x})=\Phi_{(\mathbf{x})}^\pm-\overline{\Phi}_2^\pm\ ,$$

and

$$\overline{\Phi}^\pm=\Phi_2^\pm-\Phi_1^\pm\ .$$

The shape of each of the NQR lines for $I=1$ is obtained from the corresponding frequency distribution function,[12]

$$f(\nu^\pm)=\text{const}/(d\nu^\pm/d\Psi_\pm)(d\Psi_\pm/dx)\ , \qquad (10)$$

if the modulation wave is pinned and static. If we work in the PWA[12] $(d\Psi_\pm/dx)=\text{const}$, we obtain the lineshape and position of the edge singularities in terms of the coefficients of Eqs. (7) and (8). We see from Eqs. (8)—(10) that the position of the edge singularities and the lineshape of the ν^+ must be different from that of the ν^- line except for the case where only the change in V_{zz} is different from zero. These results may be easily extended to the soliton lattice limit. In Appendix A, we show the results for the different cases appearing in the PWL.

DISCUSSION

In the structure of KCO, the cobalticyanide ions are surrounded by 12 K^+ ions while the latter are surrounded by four $Co(CN)_6{}^{3-}$ ions in such a way that each K^+ has six N atoms as nearest neighbors.[25] Each $Co(CN)_6{}^{3-}$ ion is located on the twofold axes parallel to the c axis and has almost cubic symmetry.[25] The six N atoms of a single complex anion may be separated into two N atoms roughly lined up along the b axis and four located close to the ac plane. The NQR spectrum of $20r$ and $1M$ polytypes of KCO is formed by a low-frequency doublet and a high-frequency quadruplet and may be explained by the different N-K distances present in the crystal. The KCO structure[25] at room temperature shows that the N-K distance of the—CN groups directed along b is shorter than the other N-K distances. Such difference should influence the NQR spectrum of the—CN groups directed along b as polarization, dispersion, exchange, etc., change exponentially with distance.[26] The shorter N-K distance should produce a shift toward low frequency, as found in some CN^- groups of $KCu(CN)_2$ that are coordinated at both ends.[27] Then, the low-frequency doublet could be assigned to the—CN with the shortest N-K distance while the other lines are attributed to the groups laying in the ac plane. The doublet in the $20r$ polytype disappeared below 84 K thus showing that the transition was first order instead of second order as assumed before.[17] On the other side, the lines of the—CN groups laying in the ac plane showed an entirely different behavior. One of the N sites of the ac plane showed a small but complicated splitting for the ν^- lines and a moderate one for the ν^+ lines. For all the lines of these sites, the usual negative $d\nu/dT$ value observed in other cyanides[27] was found. As seen in Fig. 2, the lines found around 2793 kHz at 77 K, and previously identified[17] as two ν^+ lines, could be identified by their shape as two-edge singularities of a single convoluted ν^+ line.[17] This result shows that the low-temperature phase of the $20r$ polytype is incommensurate[4] below 84 K. The other two ν^+ lines of the $20r$ polytype did not show signs of convolution below T_c so the IC modulation only affects one of the—CN sites of the ac plane. We found five ν^- lines at 77 K that could be grouped into a very closely spaced triplet of inequal intensity and a pair of asymmetric lines as seen in Fig. 2. As shown above, we cannot pair these lines just by comparing their lineshapes with those of the ν^+ lines. However, within the PWA,[4] the frequency difference between the edge singularities of the ν^+ and ν^+ line should have the same[4] critical exponent. The exponent[17] of the convoluted ν^+ line is $\beta=0.44$ while that of the asymmetric ν^- lines is 0.46. In contrast, the splitting of the two more intense lines of the triplet was almost temperature independent.[17] With these results in mind, it is reasonable to pair the convoluted ν^+ with the two asymmetric lines that are the edge singularities of a single ν^- line. Obviously, such lines do not correspond to two independent ν^- lines as assumed before.[17] Nakamura and coworkers[17] interpreted the transition as arising from the softening of a translational lattice mode which involves the anions and or the cations vibrating along the a or the b axis.[18] The softening of such a mode will destroy the site symmetry at the anions and will split the line from the *cis*—CN groups located near the ac plane. The NQR spectrum below T_c shows that such a destruction is not complete and instead a distribution in positions occurs and generates an IC wave that perturbs only one of the N sites located near the ac plane. The presence of two-edge singularities for each convoluted line, and their temperature dependence suggested that we were within the linear regime in the PWA[4] $[\nu_2'^\pm=0;\nu_2^\pm=0]$. If we assume that we are also in the local and constant amplitude approximation[4] and that only the symmetric or the antisymmetric component of the IC displacement is different from zero, we see that $(V_{zz}^{(1)}/2)=(\frac{1}{3}U_0)(\Delta\nu^-+\Delta\nu^+)$ and $(V_{yy}^{(1)}/2)=(\frac{1}{3}U_0)(\Delta\nu^--2\Delta\nu^+)$. Figure 3 shows the temperature dependence near T_c of $V_{zz}^{(1)}$ and $V_{yy}^{(1)}$. From Fig. 3, we see that the V_{zz} component is more sensitive to the ion displacement produced by the IC wave than V_{yy}. This result suggests that the N lone pair, that is the main contributor to V_{zz}, is perturbed by the IC wave. As pointed out above, such perturbation may arise from the interaction with the neighboring K ions.

As in $K_3Fe(CN)_6$ (KFR), we found that,[28] at room temperature, the low-frequency doublet was much broader than the other lines in samples of KCO obtained directly

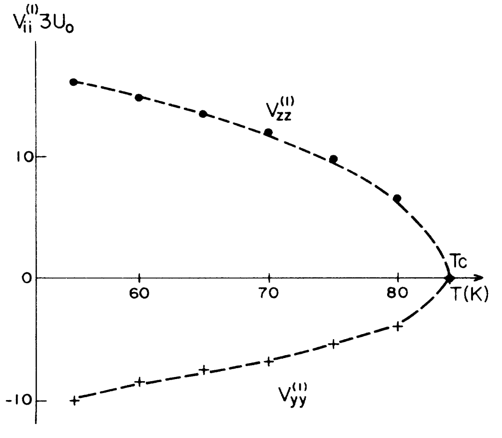

FIG. 3. Temperature dependence of the $V_{zz}^{(1)}$ and $V_{yy}^{(1)}$ as obtained from the ^{14}N NQR spectra of $K_3Co(CN)_6$ assuming that below T_c the 20*r* polytype is in the linear regime within the plane-wave approximation.

from the reaction vessel. However, the width of the doublet was reduced, upon recrystallization, toward the values found in the other lines in both polytypes. We could explain this type of broadening as in the isostructural KFR[28] by assuming that a slight disorder exists in the position K ions along one of the N-N′ directions parallel to the *b* axis. This type of disorder will produce a selective broadening of the low frequency doublet as the other N-K distances of the neighboring N atoms are only slightly changed by that type of ion displacement. Furthermore, the effect of that K disorder will be enhanced because polarization, exchange, and dispersion effects change exponentially[26] with the interatomic distances.

The existence of such a disorder in the 1*M* and 20*r* polytypes could be explained in terms of the OD structure theory[19,20] as another manifestation of the equivalence in energy of different arrangements of a given set of layers.[20] In the case of the KCO 1*M* and 20*r* polytypes, the ordered stacking sequence is approximately equivalent to that containing slightly disordered K ions so that the crystal growth conditions will determine the resulting structure.[19,20]

ACKNOWLEDGMENT

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APPENDIX

We know that for the linear case[12] ($\nu_2'^{\pm}=\nu_2'^{\pm}=0$), the frequency distribution is

$$f(\nu^{\pm})=\text{const}/[(\nu_1^{\pm})^2-(\nu^{\pm}-\nu_0^{\pm})^2]^{1/2} \tag{A1}$$

and the splitting between the edge singularities will be

$$\Delta\nu^{+}=+(\tfrac{1}{2})[(V_{zz}^{(1c)}-V_{yy}^{(1c)})^2+(V_{zz}^{(1s)}-V_{yy}^{(1s)})^2]^{1/2} \tag{A2}$$

and

$$\Delta\nu^{-}=\pm\{[V_{zz}^{(1c)}+(V_{yy}^{(1c)}/2)]^2 +[V_{zz}^{(1s)}+(V_{yy}^{(1s)}/2)^2]\}^{1/2} \tag{A3}$$

and the temperature dependence of $\Delta\nu^{\pm}=2\nu_1^{\pm}\sim(T-T_c)^{\beta}$, where β is the critical exponent. Equations (A2) and (A3) are valid for both the local and nonlocal approximations.[12,16] Similarly for the quadratic case[12] $[\nu_1^{\pm}=0,\nu_2^{\pm}\neq 0,\nu_2'^{\pm}=0]$, the frequency distribution for the local case is

$$f(\nu^{\pm})=\text{const}/[(\nu^{\pm}-\nu_0^{\pm})(\nu_2^{\pm}-\nu_0^{\pm}-\nu^{\pm})]^{1/2} \ . \tag{A4}$$

In the nonlocal case,[16]

$$f(\nu^{\pm})=\text{const}/[(\nu^{\pm}-\nu_2'^{\pm}-\nu_0^{\pm})(\nu_2^{\pm}+\nu_2'^{\pm}+\nu_0^{\pm}-\nu^{\pm})]^{1/2} \ . \tag{A5}$$

In the local approximation,[12] the edge singularities are at $\nu^{+}=\nu_0^{+}$ and

$$\nu^{+}-\nu_0^{+}=(\tfrac{1}{2})[(V_{zz}^{(2s)}-V_{yy}^{(2s)})^2+(V_{zz}^{(2c)}-V_{yy}^{(2c)})^2]^{1/2} \ ,$$

and

$$\nu^{-}=\nu_0^{-};\nu^{-}-\nu_0^{-}=\{[V_{zz}^{(2s)}+(V_{yy}^{(2s)}/2)]^2+[V_{zz}^{(2c)}+(V_{yy}^{(2c)}/2)]^2\}^{1/2} \ ,$$

while for the nonlocal case,[16]

$$\nu^{+}-\nu_0^{+}=(\tfrac{1}{2})(V_{zz}^{(2)}-V_{yy}^{(2)})-\tfrac{1}{2}[(V_{zz}^{(2c)}-V_{yy}^{(2c)})^2+(V_{zz}^{(2s)}-V_{yy}^{(2s)})^2]^{1/2} \ ,$$

and

$$\nu^{-}-\nu_0^{-}=V_{zz}^{(2)}+(V_{yy}^{(2)}/2)-\{[V_{zz}^{(2c)}+(V_{yy}^{(2c)}/2)]^2+[V_{zz}^{(2s)}+(V_{yy}^{(2s)}/2)]^2\}^{1/2} \ ;$$

the splitting will be now $\Delta\nu^{\pm}=\nu_2^{\pm}\sim(T-T_c)^{2\beta}$. For the linear plus quadratic terms,[12] we have two singularities in the local case given by

$$\nu_{(a)}^{+}-\nu_0^{+}=\tfrac{1}{2}[(V_{zz}^{(1c)}-V_{yy}^{(1c)})^2+(V_{zz}^{(1s)}-V_{yy}^{(1s)})^2]^{1/2}+\tfrac{1}{2}[(V_{zz}^{(2c)}-V_{yy}^{(2c)})^2+(V_{zz}^{(2s)}-V_{yy}^{(2s)})^2]^{1/2}$$

and

$$\nu^{-}_{(a)}-\nu^{-}_{0}=\{[V^{(1c)}_{zz}+(V^{(1c)}_{yy}/2)]^2+[V^{(1s)}_{zz}+(V^{(1s)}_{yy}/2)]^2\}^{1/2}$$
$$+\{[V^{(2s)}_{zz}+(V^{(2s)}_{yy}/2)]^2+[V^{(2c)}_{zz}+(V^{(2c)}_{yy}/2)]^2\}^{1/2}\ .$$

We have also singularities for $\nu^{+}_{(b)}-\nu^{+}_{0}=-\nu^{+}_{1}+\nu^{+}_{2}$ if

$$|[(V^{(1c)}_{zz}-V^{(1c)}_{yy})^2+(V^{(1s)}_{zz}-V^{(1s)}_{yy})^2]^{1/2}|<2|[(V^{(2c)}_{zz}-V^{(2c)}_{yy})^2+(V^{(2s)}_{zz}-V^{(2s)}_{yy})^2]^{1/2}|\ ,$$

while for the ν^{-} lines, the condition is

$$|\{[V^{(1c)}_{zz}+(V^{(1c)}_{yy}/2)]^2+[V^{(1s)}_{zz}+(V^{(1s)}_{yy}/2)]^2\}^{1/2}<2|\{[V^{(2c)}_{zz}+(V^{(2c)}_{yy}/2)]^2+[V^{(2s)}_{zz}+(V^{(2s)}_{yy}/2)]^2\}^{1/2}|\ .$$

The frequency distribution is given in this case[12] by

$$f(\nu^{\pm})=f^{\pm}(\Phi^{\pm}_{A})$$
$$\text{for } \nu^{\pm}-\nu^{\pm}_{1}+\nu^{\pm}_{2}<\nu^{\pm}<\nu^{\pm}_{2}+\nu^{\pm}_{1}+\nu^{\pm}_{2}\ , \qquad \text{(A6)}$$
$$f(\nu^{\pm})=f^{\pm}(\Phi_{A})+f(\Phi_{B})$$
$$\text{for } \nu^{\pm}_{0}-[(\nu^{\pm}_{1})^2/4\nu^{\pm}_{2}]<\nu^{\pm}<\nu^{\pm}_{0}-\nu^{\pm}_{1}+\nu^{\pm}_{2}\ , \qquad \text{(A7)}$$

where

$$f(\Phi)=\text{const}/|\sin\Phi(\nu^{\pm}_{1}+2\nu^{\pm}_{2}\cos\Phi)|$$

with

$$\cos\Phi_{A,B}=\{-\nu^{\pm}_{1}\pm[(\nu^{\pm}_{1})^2+4(\nu^{\pm}-\nu^{\pm}_{0})\nu^{\pm}_{2}]^{1/2}\}/2\nu^{\pm}\ .$$

For the nonlocal case,[16] we know that if $|\nu^{\pm}_{2}/\nu^{\pm}_{1}|<\frac{1}{2}$, we obtain only two-edge singularities while if $|\nu^{\pm}_{2}/\nu^{\pm}_{1}|=\frac{1}{2}$ and $\Phi=+90°$ or 0°, we have three-edge singularities. For $\frac{1}{2}<|\nu^{\pm}_{2}/\nu^{\pm}_{1}|<1$, $\Phi=90°$ or 0°, we have four-edge singularities at lower temperature. For $\Phi=45°$, an additional singularity appears at $|\nu^{\pm}_{2}/\nu^{\pm}_{1}|=1$ between the two-edge singularities.

The above results may be easily generalized to spins $I>\frac{3}{2}$ if relationships similar to those of Eqs. (1) and (2) are used.

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