

Electron spin resonance in a two-dimensional compound with appreciable interplane coupling: NaCrS_2 [†]

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Measurements of the electron-spin-resonance (ESR) linewidth ΔH in NaCrS_2 are presented and compared with the theory of Richards and Salamon for ESR in two dimensions (2d). NaCrS_2 was chosen because it is a layer compound with a ferromagnetic intraplane interaction J and a sizable antiferromagnetic interplane interaction J' ($|J'/J| = 1/6$). Previously the most detailed study of ESR which paid specific attention to the 2d feature of the spin dynamics was for K_2MnF_4 , which has negligible J' and an antiferromagnetic J ; so it is of interest to compare the two systems. ΔH in NaCrS_2 does not have a minimum at $3 \cos^2 \theta = 1$ ($\theta =$ angle of field with respect to c axis), in contrast to the situation in K_2MnF_4 . This feature is explained by the effect of interplane coupling. The theory, modified to account for interplane exchange, also correctly gives the high-temperature ratio $\Delta H(\theta = 0)/\Delta H(\theta = 90^\circ) = 1.6$. The measured peak-to-peak linewidth at $\theta = 0$ and room temperature, $\Delta H = 80$ Oe, is smaller than the calculated 125 Oe. ΔH increases continuously as the temperature T is lowered in a manner described reasonably well by theory. Here agreement is much better than in some other planar ferromagnets which possibly have more nondipolar broadening mechanisms than NaCrS_2 . The anisotropy $\Delta H(\theta = 0)/\Delta H(\theta = 90^\circ)$ decreases as the temperature is lowered, which is in contradiction to theory for a fixed J'/J and to results on other quasi-2d compounds and may be indicative of J'/J being temperature dependent.

I. INTRODUCTION

Magnetically quasi-two-dimensional (2d) layer compounds have been studied extensively for the past few years.¹ The interest has focused largely on the peculiarities of statistical mechanics of the 2d Heisenberg model, which may² have a finite critical temperature T_c although it cannot³ possess long-range order below T_c . It has been possible^{4,4} to investigate the effects of interplane coupling, which ultimately makes the system 3d, upon critical phenomena and the "cross over" from 2d to 3d critical exponents. This has come about because of the availability of compounds which vary between the examples of K_2NiF_4 or K_2MnF_4 for which⁵ $J'/J < 3 \times 10^{-3}$ (J and J' are the intraplane and interplane exchange interactions, respectively) and of compounds for which J'/J is not negligible (the present subject, NaCrS_2 has $|J'/J| = \frac{1}{6}$ at 4°K).⁶

Recent experimental and theoretical work has shown that exchange-narrowed electron spin resonance (ESR) has remarkably different characteristics in 1d or 2d than in 3d even at the highest temperatures.⁷ In particular, the reader is referred to a detailed treatment,⁸ henceforth referred to as I, in which the linewidth ΔH and line shape were calculated for an *ideal* 2d system and excellent agreement was obtained with experiments on K_2MnF_4 . The main features observed and ex-

plained in I were (i) an angular dependence roughly of the form $\Delta H = a + b(3 \cos^2 \theta - 1)^2$, where a and b are appropriate constants and θ is the angle of applied field with respect to the c axis perpendicular to the plane, and (ii) a temperature (T) dependence such that ΔH initially decreases as T is lowered from room temperature. It was pointed out that both effects are anomalous for conventional 3d exchange narrowing, assuming—as is correct for K_2MnF_4 —that ΔH is caused by dipolar interactions and that J is antiferromagnetic.

Although agreement between theory and experiment has been very good for K_2MnF_4 and other 2d antiferromagnets,⁹ the situation is less than satisfactory in compounds where the intraplanar coupling is ferromagnetic. As remarked in I, one expects ΔH initially to increase as T is lowered for the 2d ferromagnet, whereas experiments^{10,11} on K_2CuF_4 and NiCl_2 show a nearly linear $\Delta H \propto T$ relation at high temperature. The results in the former compound are particularly disturbing since it is isomorphous to K_2MnF_4 . One possible source of difficulty in applying the results of I to K_2CuF_4 and other compounds is that the broadening mechanism may not be strictly dipolar for non- S -state ions. In fact, there is strong evidence for this in K_2CuF_4 , where the dipole interaction accounts for only 30% of the observed anisotropy field¹² at low tempera-

tures. The dominant broadening interaction is then likely to be anisotropic exchange, which can have a strong temperature dependence¹³ at high T and thus complicate the analysis.

It is therefore desirable to study a quasi-2d compound with a ferromagnetic J in which the anisotropic part of the interaction is dominantly dipolar. NaCrS_2 , which has a ferromagnetic $J = 3.1^\circ\text{K}$, appears to be a fairly good candidate in this respect. Elliston¹⁴ has shown that anisotropy of the field required for resonance at high temperature is adequately accounted for by the dipolar fields. Also, the Cr^{3+} -ion g tensor in NaCrS_2 should show negligible anisotropy, as has been observed by EPR in the isomorphous NaInS_2 on Cr^{3+} impurities substituting for In^{3+} ions with $g_1 \cong g_0 = 1.983 \pm 0.001$.¹⁵ The small anisotropy of local behavior in this layer compound is also reflected in the splitting parameter D which is 5.2 times smaller than in trigonal ruby. This has been ascribed to ligand field compensating effects of the out-of-plane distorted sulfur octahedron and the nearest-neighbor in-plane In^{3+} ions.¹⁵

A second question concerns the $(3 \cos^2 \theta - 1)^2$ feature of the angular dependence, which is not always observed. In NiCl_2 , for example, ΔH is isotropic at room temperature.¹¹ Since the minimum in ΔH at $\theta = \cos^{-1}(1/\sqrt{3}) \approx 55^\circ$ is a direct consequence of 2d spin correlations,⁸ it is of interest to see how this is altered by interplane interactions. Once again, NaCrS_2 is well suited for this study since it has a measurable antiferromagnetic $J' \approx \frac{1}{6}J$.

The temperature and angular dependence of ΔH in NaCrS_2 are reported in this paper and compared with calculations based on finite interplane coupling. The temperature dependence, which is in qualitative agreement with the ideas of I, has previously been studied¹⁴; but emphasis was placed primarily on behavior near the Néel temperature T_N and no comparison was made with a theory which accounts for the quasi-2d character. The full angular dependence, not given by Elliston,¹⁴ more nearly resembles $a + b \cos^2 \theta$ than $a + b(3 \cos^2 \theta - 1)^2$. The disappearance of the minimum at 55° is shown to be a consequence of the interplane coupling. We are able to calculate ΔH at room temperature to within better than a factor of 2 without any adjustable parameters. Experimental results are presented in Sec. II followed by the theory of Sec. III.

II. EXPERIMENT

Measurements of the absorption derivative were made with conventional X - and K -band spectrometers operating at 9.5 and 23.4 GHz, respectively. Thin-plate-like samples of the hexagonal material,

similar to the ones used in Ref. 6, were grown from sodium polysulfide fluxes¹⁶ and provided by H. J. Scheel. They are polycrystalline within the plane of the plate but have a common (to within about 1°) c axis perpendicular to the plate.

Figure 1 shows angular dependence of the peak-to-peak width ΔH at high temperature. The main features of note are that there is only a small trace of a $(3 \cos^2 \theta - 1)^2$ component and that ΔH is essentially independent of frequency between X band and K band. The line shape in the nearly ideal 2d compound K_2MnF_4 was shown in I to be non-Lorentzian at $\theta = 0$ but Lorentzian at $\theta = 55^\circ$. Here, the line is Lorentzian at $\theta = 0^\circ$, 55° , and 90° out to at least three peak-to-peak widths on either side of the resonance field. As explained in Sec. III, one should expect a Lorentzian line at all angles for the magnitude of interplane coupling present in NaCrS_2 .

Temperature dependence of the linewidth at $\theta = 90^\circ$ is given in Fig. 2, while Fig. 3 shows how the anisotropy $\Delta H(\theta = 0)/\Delta H(\theta = 90^\circ)$ varies with T . The ratio $\Delta H(\theta = 55^\circ)/\Delta H(\theta = 90^\circ)$ was independent of temperature to within experimental error, in contrast to $\Delta H(\theta = 0)/\Delta H(\theta = 90^\circ)$, which shows a definite downward trend at the lower temperatures.

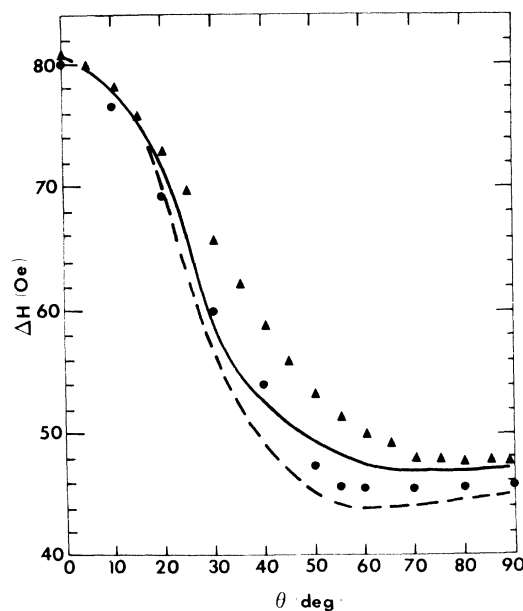


FIG. 1. Angular dependence of room-temperature peak-to-peak linewidth; \blacktriangle , 9.5 GHz; \bullet , 23.4 GHz. Solid curve—theory, 9.5 GHz, normalized to $\Delta H = 80$ Oe at $\theta = 0$. Dashed curve—theory, 23.4 GHz, normalized to $\Delta H = 80$ Oe at $\theta = 0$. Data were also taken at points $180^\circ - \theta$ to check on symmetry and sample alignment. They agreed with the points at θ to within 1 Oe or better at all angles.

III. THEORY

A. General description

The underlying theory and method of calculation for ESR linewidth in an ideal 2d compound were presented in I. Here we briefly review some of the basic concepts and discuss those modifications which result from the inclusion of interplane coupling. The starting formula is

$$\frac{\chi''(\omega - \omega_0)}{\omega} \propto \mathcal{F} \left[\exp \left(- \sum_{M=0}^2 \int_0^t d\tau \right. \right. \\ \left. \left. \times (t - \tau) g_M(\tau) \cos M\omega_0\tau \right) \right] \quad (1)$$

in which $\chi''(\omega - \omega_0)$ is the absorption at angular frequency ω when the resonance frequency is ω_0 , \mathcal{F} indicates the Fourier transform at the frequency ω , and $g_M(\tau)$ is a four-spin correlation function corresponding to that part of the dipolar interaction which induces a change $\pm M$ in Zeeman quantum number. For diffusion in 2d, $g_M(\tau)$ is proportional to τ^{-1} for long times so that the upper limit of the integral cannot be extended to ∞ for $M=0$, and the line shape, being related to $\mathcal{F}[\exp(-t \ln t)]$, can be non-Lorentzian. In a real compound, however, there is a characteristic time t_0 beyond which interplane diffusion becomes important and $g(\tau)$ decays as $\tau^{-3/2}$, i. e., diffusively for 3d. If t_0 is much less than the ESR relaxation time $(\gamma\Delta H)^{-1}$

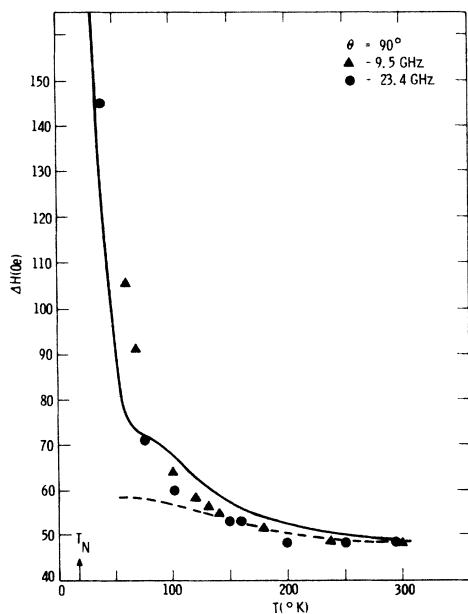


FIG. 2. Linewidth vs temperature at $\theta = 90^\circ$. Solid curve is theory including static interplane correlations. Dashed curve includes only ferromagnetic intraplane static correlations. Both curves are normalized to 48.5 Oe at 300°K.

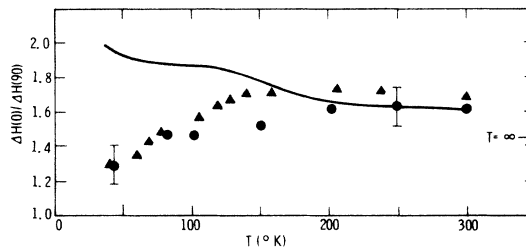


FIG. 3. Linewidth anisotropy $\Delta H(0)/\Delta H(90)$ vs temperature; \blacktriangle , 9.5 GHz; \bullet , 23.4 GHz. Solid curve is theoretical, without any adjustable parameters. Theoretical $T = \infty$ point is marked.

(γ is the gyromagnetic ratio), then the upper limit in (1) can be extended to infinity, and the line shape becomes Lorentzian with a width given by

$$\gamma\Delta H = \frac{2}{\sqrt{3}} [\bar{g}_0(0) + \bar{g}_1(\omega_0) + \bar{g}_2(2\omega_0)], \quad (2)$$

where $\bar{g}_M(\omega)$ is the Fourier transform of $g_M(\tau)$ and the factor of $2/\sqrt{3}$ has been inserted to convert halfwidth to peak-to-peak derivative width for a Lorentzian.

The concept of a finite time t_0 for crossover to 3d behavior and its effect on line shapes for linear-chain compounds has been treated elsewhere.^{17,18} We assume that the condition $\gamma\Delta H_0 t_0 \ll 1$ is satisfied for NaCrS₂, and proceed to work with Eq. (2). A numerical estimate of t_0 which supports this conclusion will be given later.

Before treating details of the theory, it may be instructive to see qualitatively how angular and temperature dependence are related to the relative values of ω_0 , t_0 , and J . Referring to Fig. 4, the initial decay of $g_M(\tau)$ takes place in a time τ_c of the order of \hbar/J . The function $g_M(\tau)$ consists

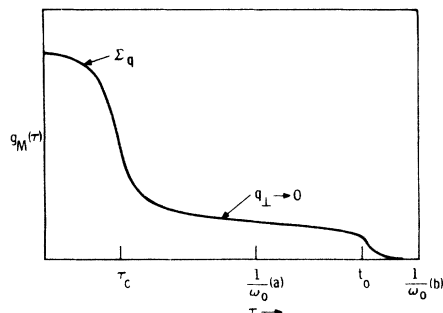


FIG. 4. Schematic of correlation function $g_M(\tau)$ showing pertinent times τ_c , t_c , and $1/\omega_n$. The initial decay is governed by equal contributions from all modes (Σq), while the long-time diffusive part is controlled by long in-plane wavelength modes ($q_1 \rightarrow 0$). See text for further explanation.

of a sum over \vec{q} of spin-time correlation functions at wave vector \vec{q} , weighted by dipolar factors [see Eq. (3)]. At high temperature all \vec{q} 's contribute equally to the correlation functions for short times. As noted in I, this gives rise to an angular dependence which would make $\Delta H(\theta=0) < \Delta H(\theta=90^\circ)$ if one considered short-time effects only (see Fig. 2 of I). The τ^{-1} diffusive tail exists for times roughly between τ_c and the cutoff time t_0 . In this region, as shown in I, angular dependence is dominated by $q_\perp=0$ (q_\perp is the component of \vec{q} in the plane). Thus, if $t_0 \gg \tau_c$ we can still expect the modes with long wavelengths in the plane to be dominant. Consider now ω_0 . If $\omega_0 t_0 \gg 1$, as in case (a) of Fig. 4, then only the secular part ($M=0$) will persist for the longer times since the longtime effect of $M \neq 0$ will be killed by the $\cos M\omega_0\tau$ modulation in (1). It is this feature, which holds in the ideal 2d system where $t_0 \rightarrow \infty$, which produces the $(3 \cos^2 \theta - 1)^2$ character to ΔH since this is the angular dependence of the $q_\perp=0$ part of $g_{M=0}$. (We assume throughout that inter-plane dipolar coupling is negligible.) If, however, $\omega_0 t_0 \ll 1$, as in (b) of Fig. 4, then all M values contribute equally for $\tau \leq t_0$. The angular dependence will then be reflected by the $q_\perp=0$ (still assuming $t_0 \gg \tau_c$) part of $g_0 + g_1 + g_2$, whose angular dependence may be shown to be $1 + \cos^2 \theta$. The angular variation of ΔH for various cases, as predicted on the basis of this discussion, is summarized in Table I. The main point to note is that, for a given $J(\tau_c^{-1})$ and ω_0 , the qualitative behavior of $\Delta H(\theta)$ can be quite sensitive to the relative position of the cutoff time t_0 . Values of τ_c^{-1} , t_0^{-1} , and ω_0 appropriate to NaCrS₂ are given in Table II.

The temperature dependence is affected by the ratio t_0/τ_c but is not particularly influenced by ω_0 . If $t_0 \approx \tau_c$ then short-time behavior dominates and, as shown in I, a dependence roughly of the form $\Delta H \propto (\chi_0 T)^{-1}$ is expected; but if $t_0 \gg \tau_c$ so that the long-wavelength modes are the controlling factor, then roughly the opposite dependence, $\Delta H \propto \chi_0 T$, should be seen, also as pointed out in I. Whether the ferromagnetic planes ultimately order in 3d ferromagnetically or antiferromagnetically makes no qualitative difference in ΔH . The linewidth should diverge at the critical temperature in either case, at least in the limit of zero applied field H . For complete ferromagnetic ordering in 3d, as with

TABLE I. Linewidth anisotropy for various relative values of τ_c , t_0 , ω_0 (see Fig. 4).

| $\tau_c \approx t_0$ | $\Delta H(0) < \Delta H(90)$ | |
|---------------------------------|---|---|
| $\tau_c \ll 1/\omega_0 \ll t_0$ | $\Delta H(0) > \Delta H(90) > \Delta H(55)$ | $\{(3 \cos^2 \theta - 1)^2 \text{ character}\}$ |
| $\tau_c \ll t_0 \ll 1/\omega_0$ | $\Delta H(0) > \Delta H(55) > \Delta H(90)$ | $\{1 + \cos^2 \theta \text{ character}\}$ |

TABLE II. Values of characteristic rates for NaCrS₂ (see Fig. 4).

| |
|--|
| $\tau_c^{-1} = 3.2 \times 10^{12} \text{ sec}^{-1}$ ^a |
| $t_0^{-1} = 4.8 \times 10^{10} \text{ sec}^{-1}$ ^b |
| $\omega_0 = 6.0 \times 10^{10} \text{ sec}^{-1}$ ^c |

^aCalculated from $\tau_c^{-1} = \omega_e/\sqrt{2}$, with $\omega_e^2 = \frac{16}{3} J^2 Z S(S+1)$ [see Eqs. (C1), (C3), and (C4) of I].

^b $t_0^{-1} = D'/c^2$, with D' given by Eq. 12.

^cAt 9.5 GHz.

K₂CuF₄, there is the additional complication that H suppresses the critical fluctuations and can remove the divergence.

B. Correlation functions and susceptibility

An advantage of Eq. (2) is that one can work directly with frequency components $\tilde{g}_M(\omega)$. This was not possible in I, where an approximate analytic expression for $g_M(\tau)$ was used in order to perform the integration. We estimate $\tilde{g}_M(\omega)$ as follows. Upon making the usual decoupling approximation, $g_M(\tau)$ reduces to the form⁸

$$g_M(\tau) \propto f_0^{-1} N^{-1} \sum_q |F_q^{(M)}|^2 \langle S_q^z(\tau) S_{-q}^z(0) \rangle^2 / [\frac{1}{3} S(S+1)]^2, \quad (3)$$

in which $F_q^{(M)}$ is a dipole factor at the wave vector q , N is the total number of spins, $\langle S_q^z(\tau) S_{-q}^z(0) \rangle$ is the two-spin time correlation function and f_0 is $\chi_0 T$ (χ_0 = static susceptibility) normalized to its infinite temperature value. It was shown recently,¹⁹ in a publication referred to as II, that

$$\langle S_q^z(\tau) S_{-q}^z(0) \rangle^2 = \langle \vartheta_q(\tau) \vartheta_{-q}(0) \rangle, \quad (4)$$

[see Eq. (A4) of II] where

$$\vartheta_q \equiv S_q^z S_{-q}^z - \langle S_q^z S_{-q}^z \rangle. \quad (5)$$

As in II we assume that the Fourier transform $\langle \vartheta_q \vartheta_{-q} \rangle_\omega$ is represented by a generalized diffusivity²⁰ in the same manner as $\langle S_q^z S_{-q}^z \rangle_\omega$,

$$\langle \vartheta_q \vartheta_{-q} \rangle_\omega = \frac{\langle S_q^z S_{-q}^z \rangle^2 \tilde{D}_q(\omega)}{\omega^2 [1 + \tilde{Q}(\omega)]^2 + [\tilde{D}_q(\omega)]^2}, \quad (6)$$

[Fourier transforms are defined here and in Eq. (2) without factors involving 2π] in which $\tilde{D}_q(\omega)$ is the generalized diffusivity and $\tilde{Q}(\omega)$ is a principal part integration defined in II. The assumption of a Gaussian frequency dependence of $\tilde{D}_q(\omega)$ then leads, as shown in II, to

$$\tilde{D}_q(0) = (2\pi)^{1/2} \langle \omega_q^2 \rangle^{3/2} / (\langle \omega_q^4 \rangle + \langle \omega_q^2 \rangle^2)^{1/2}, \quad (7)$$

$$\tilde{Q}_q(0) = -2\pi^{-1/2} \tilde{D}_q(0) \tilde{\Gamma}_q, \quad (8)$$

where

$$\tilde{\Gamma}_q = [\frac{1}{2} \langle \omega_q^2 \rangle / (\langle \omega_q^4 \rangle + \langle \omega_q^2 \rangle^2)]^{1/2} \quad (9)$$

is the characteristic time for the decay of $\bar{D}_q(\omega)$. In the above $\langle \omega_q^2 \rangle$ and $\langle \omega_q^4 \rangle$ are the second and fourth moments, respectively, of $\langle S_q^z S_{-q}^z \rangle_\omega$. If $\omega \bar{\Gamma}_q \ll 1$ it is permissible to replace $\bar{D}_q(\omega)$ and $\bar{Q}(\omega)$ in (6) by their zero-frequency values (7) and (8). Since $\omega \bar{\Gamma}_q$ is of the order of $\hbar \omega / J [ZS(S+1)]^{1/2}$ this simplification is well justified for NaCrS₂ at K band and lower frequencies (Z is the number of neighbors, 6 for the NaCrS₂ lattice).

Evaluation of the moments²¹ in Eq. (7) shows that for $q \rightarrow 0$ the diffusivity reduces to

$$\bar{D}_q(0) = 2(Dq_1^2 + D'q_2^2), \quad (10)$$

where q_1 and q_2 are components of \vec{q} in and perpendicular to the plane, respectively, and where

$$D = \frac{1}{2}(\frac{1}{2}3\pi)^{1/2} |J| [S(S+1)]^{1/2} a^2 / \hbar, \quad (11)$$

$$D' = (\frac{1}{2}3\pi)^{1/2} |J'|^2 / J [S(S+1)]^{1/2} c^2 / \hbar, \quad (12)$$

for the NaCrS₂ lattice in which the six nearest neighbors at a distance a in the plane are coupled by J and the six nearest neighbors in adjacent planes are coupled by J' , with c being the interplane distance. Equations (11) and (12) are valid at infinite temperature to lowest order in J'/J and for $S(S+1) \gg \frac{3}{8}$. The basic form (10) is an obvious extension of the well-known result $\bar{D}_q(0) = Dq^2$ to an anisotropic system and follows directly from the moments.

The dependence $D' \propto |J'|^2/J$ for $J'/J \ll 1$ is a consequence of the assumed dependence (7) of the anisotropic diffusion coefficient upon moments in the case of weak interplane coupling. This relation is known^{17,18} to break down in quasi-1d systems where $D_2 \propto |J_2^{4/3}/J_1^{1/3}|$ is the interchain diffusion rate when J_1 and J_2 are the intraplane and interchain couplings, respectively. Similarly one may expect, on the basis of 2d time correlations, that $D' \propto |J'|^2/J [\ln(|J'/J|^2) - 1]$ is more nearly correct for the interplane diffusion. The logarithmic correction is not overly serious and will be ignored here so that the forms (7)–(9) can be maintained. However, it will be noted later on in making numerical comparison with the observed line-widths.

The characteristic time t_0 for interplane diffusion is important and is of the order of D'/c^2 . For $\Delta H = 80$ Oe, $J/k_B = 3.1$ °K = $6|J'|/k_B$, we have $\gamma \Delta H t_0 = 0.03 \ll 1$, so that the assumption leading to Eq. (2) is well justified.

Temperature dependence in Eqs. (6)–(9) is accounted for by letting

$$\langle S_q^z S_{-q}^z \rangle = \frac{1}{3} S(S+1) f_q, \quad (13)$$

where f_q is $\langle S_q^z S_{-q}^z \rangle \propto \chi_q T$ normalized to its $T \rightarrow \infty$ value. Since, for example, in $\langle \omega_q^2 \rangle = - \langle \ddot{S}_q^z S_{-q}^z \rangle / \langle S_q^z S_{-q}^z \rangle$, the numerator is much less strongly dependent on temperature than the denominator, it

is sufficient to take

$$\langle \omega_q^2 \rangle = \langle \omega_q^2 \rangle_\infty / f_q, \quad (14)$$

and similarly,

$$\langle \omega_q^4 \rangle = \langle \omega_q^4 \rangle_\infty / f_q, \quad (15)$$

where $\langle \omega_q^2 \rangle_\infty$ and $\langle \omega_q^4 \rangle_\infty$ are the infinite temperature limits found in Ref. 20. Examination of Fig. 4(a) of I shows that (14) and (15) are indeed quite reasonable over the range of interest. By analogy with the work of Lee and Liu²² and of Lines²³ we use the form

$$f_q = \frac{f_0 + \frac{1}{2}(f_0 - f_s)(1 - \gamma'_q)}{1 + \lambda \Omega_q^2}, \quad (16)$$

in which f_0 is the $q=0$ value, proportional to $\chi_0 T$ where χ_0 is the observed static susceptibility; f_s is the value at the staggered, antiferromagnetic mode of 3d order (ferromagnetic planes, antiferromagnetically coupled); $\gamma'_q = (1/Z') |\sum_{\langle j \rangle} e^{i\vec{q} \cdot \vec{r}_{ij}}|$ where the sum runs over the $Z'=6$ nearest neighbors in adjacent planes;

$$\Omega_q^2 = (1 - \gamma_q)^2 + 2|J'/J|(1 - \gamma_q) + |J'/J|^2(1 - \gamma_q'^2)$$

is proportional to the square of the spin-wave frequency²⁴ in the 3d ordered state, where $\gamma_q = (1/Z) \sum_{\langle j \rangle} e^{i\vec{q} \cdot \vec{r}_{ij}}$ is a sum over the $Z=6$ nearest neighbors in the plane.

Equation (16) is the same as used in I except for modifications required by the interplane coupling and different nature of the 3d order. It has the standard Ornstein-Zernicke dependence on \vec{q} for small values of $\vec{q} - \vec{q}_0$, where \vec{q}_0 is the superlattice vector for antiferromagnetic ordering of the ferromagnetic planes ($\gamma_{q_0} = 1$, $\gamma'_{q_0} = -1$), and is the result of random-phase-approximation (RPA) Green's function theories generalized to include the type of 3d order found in NaCrS₂. Note that the parameters f_0 and f_s are introduced so as to make $f_q = f_0$, f_s at $\vec{q} = 0$, \vec{q}_0 since $\Omega_{q_0} = \Omega_0 = 0$. The presence of Ω_q^2 in the denominator, which produces the Ornstein-Zernicke behavior, is consistent with the notion²³ that, near a phase transition, the \vec{q} dependence of the fluctuations is a reflection of the spin-wave modes in the ordered state. The quantity λ , which is related to the inverse correlation length, may also be computed from the RPA. Alternatively, it can be fixed so as to satisfy the sum rule $N^{-1} \sum_q f_q = 1$ at high temperatures where the correlations are isotropic. Since we are interested in sums over the full zone, we find it desirable, as in I, to maintain the sum rule and calculate λ accordingly. An adequate approximation is

$$\lambda = [\frac{1}{2}(f_s + f_0) - 1] (1 + |J'/J|)^{-2},$$

which results from expanding $(1 + \lambda \Omega_q^2)^{-1}$ in powers of γ_q , γ'_q and noting that $\sum_q \gamma_q = \sum_q \gamma'_q = 0$. It satis-

fies the sum rule to within better than 10% at all temperatures considered.

The quantity f_0 is obtained from the susceptibility data of Blazey and Rohrer.⁶ We assume that f_s can be written as

$$f_s = f_0(1 - T_N/T)^{-1}, \quad (17)$$

where $T_N = 18^\circ\text{K}$ is the 3d ordering temperature. The factor $(1 - T_N/T)^{-1}$ produces a mean-field divergence of the antiferromagnetic mode, while the prefactor f_0 insures that f_q in (16) is independent of components of \vec{q} perpendicular to the plane in the case of no interplane coupling ($J' = T_N = 0$). Since we are not concerned here with precise values of critical exponents, the above should give an adequate semiquantitative description of the onset of critical fluctuations in 3d.

C. Calculation of linewidth

The linewidth is given by Eq. (2). From the expressions in Sec. III it is evident that

$$\begin{aligned} \tilde{g}_M(\omega) = & f_0^{-1} N^{-1} \sum_q |F_q^{(M)}|^2 \\ & \times \frac{f_q^2 \tilde{D}_q(0)}{\omega^2 [1 - 2\pi^{-1/2} \tilde{D}_q(0) \tilde{\Gamma}_q]^2 + [\tilde{D}_q(0)]^2}, \quad (18) \end{aligned}$$

where f_q , $\tilde{D}_q(0)$, and $\tilde{\Gamma}_q$ are found in Eqs. (16), (7), (9), (14), and (15). It remains to discuss the dipole factors $F_q^{(M)}$, which are given explicitly in I. They are of the form

$$F_q^{(M)} \propto \sum_j r_{ij}^{-3} Y_2^M(\theta_{ij}, \varphi_{ij}) e^{i\vec{q} \cdot \vec{r}_{ij}}, \quad (19)$$

where θ_{ij} and φ_{ij} are polar and azimuthal angles of \vec{r}_{ij} with respect to the applied field and Y_2^M is the spherical harmonic. The effect of interplane dipolar interactions should be negligible in NaCrS_2 since the closest distance to a spin in an adjacent plane, $(c^2 + \frac{1}{3}a^2)^{1/2}$, is 1.93 times the intraplane distance a —which is in fact more favorable than the comparable figure of 1.72 for K_2MnF_4 —so the summation in (19) is confined to a plane. To avoid lengthy summations of (18) over a hexagonal Brillouin zone, we replace $F_q^{(M)}$ by an angular average. That is, for example,

$$\langle e^{i\vec{q} \cdot \vec{r}_{ij}} \rangle_{\text{av}} = J_0(q_\perp r)$$

for the summation over sites at a distance r , where J_0 is the zeroth-order Bessel function. Similarly, using the coordinates in Fig. 1 of I, we find

$$\begin{aligned} \langle (3 \cos^2 \theta_{ij} - 1) e^{i\vec{q} \cdot \vec{r}_{ij}} \rangle_{\text{av}} \\ = [\frac{1}{2}(1 - 3 \cos^2 \theta) J_0(q_\perp r) - \frac{3}{2} \sin^2 \theta \cos 2\varphi_q J_2(q_\perp r)], \end{aligned}$$

with related expressions for the sums involving $Y_2^{(1)}$ and $Y_2^{(2)}$, where φ_q is the angle of \vec{q}_\perp with respect to the H, c plane.

In the same spirit we set

$$\gamma_q = J_0(q_\perp a),$$

and

$$\gamma'_q = J_0(q_\perp a / \sqrt{3}) \cos q_z c.$$

A further simplification in computing $F_q^{(M)}$ is to replace the sum over all sites beyond the nearest neighbors by an integration. Thus, for example, we take

$$\sum_j r_{ij}^{-3} e^{i\vec{q} \cdot \vec{r}_{ij}} = \frac{6}{a^3} J_0(q_\perp a) + \frac{4\pi}{\sqrt{3} a^2} \int_{r_0}^{\infty} \frac{dr}{r^2} J_0(q_\perp r),$$

with $r_0 = (9\sqrt{3}/2\pi)^{1/2} a$ chosen so that a circle of radius r_0 has the same area as the hexagon described by the next-nearest neighbors at the distance $\sqrt{3}a$. Comparison with exact lattice summations for $F_{q=0}^{(M)}$, $N^{-1} \sum_q |F_q^{(M)}|^2$, and $N^{-1} \sum_q \gamma_q^2$ showed that these quantities were estimated to within better than 6% by the above scheme.

This method of approximating F_q allows the summation (18) to be reduced to an integral over a cylindrical Brillouin zone, and, further, the angular, φ_q , part of the integration is trivial since only $F_q^{(M)}$ depends on φ_q . Hence, the numerical Brillouin-zone integration was only over the variables q_\perp and q_z . Numerical values needed for the calculation of ΔH are $a = 3.53 \text{ \AA}$, $J/k_B = 3.1^\circ \text{K}$, $J'/k_B = -0.5^\circ \text{K}$, $\gamma = 1.75 \times 10^7 \text{ sec}^{-1} \text{G}^{-1} (g = 1.98)$.

IV. THEORETICAL RESULTS AND COMPARISON WITH EXPERIMENT

The linewidth at $\theta = 0$ was calculated to be $\Delta H(0) = 105 \text{ Oe}$ at infinite temperature and 125 Oe at 300°K , whereas the measured value is 80 Oe at room temperature. This absolute agreement, without any adjustable parameters, is fairly good as far as calculations of exchange-narrowed ESR are generally concerned, but it is not as good as found in I for K_2MnF_4 .

The lines in Fig. 1 show the predicted angular dependence at 300°K for the two frequencies, where the theoretical curves have been normalized to 80 Oe at $\theta = 0$. Good agreement is seen. Note that the theoretical curve has no minimum at 55° for 9.5 GHz and only a slight one for 23.4 GHz . The relatively small ($\lesssim 10\%$) predicted frequency dependence is borne out by the data, particularly for $\theta \gtrsim 55^\circ$.

One possible source of discrepancy in the absolute value of ΔH is the expression (12) for the interplane diffusion coefficient D' . As mentioned in the discussion following Eq. (12), this moments formula may underestimate D' by a factor of $\ln(|J/J'|^2) - 1 = 2.6$. As a first approximation we could account for this by using an effective J' which is larger by a factor of $(2.6)^{1/2}$. Figure 5 shows how $\Delta H(0)$ and $\Delta H(0)/\Delta H(90)$ depend on $|J'/J|$ at in-

finite temperature. If $|J'/J|$ were increased to $(2.6)^{1/2}/6 = 0.27$, $\Delta H(0)$ would decrease to 80 Oe, but it would be at the expense of considerably worsening the agreement with the anisotropy. The reason for this can be seen from Fig. 4 and Table I: as $|J'/J|$ increases there is a decrease in t_0/τ_c and thus a movement toward the short-time angular dependence.

The solid curve in Fig. 2 shows the predicted temperature dependence at 90° using the full $3d$ correlation of Eq. (16), while the dashed curve is calculated assuming purely $2d$ correlations [$f_0 = f_s$ in (16) and $J' = 0$ in the expressions for ω_q and λ]. Above 140°K , the pure $2d$ model gives a better fit, although the difference between the curves is less than 10%. Below about 80°K the effect of critical interplane fluctuations is strongly manifested, and the theory is in reasonable accord with the point at which ΔH begins to increase rapidly. The shoulder in the theoretical curve at 80°K is caused by a maximum in the observed $\chi_0 T$ at that point.

The solid curve in Fig. 3 shows the predicted anisotropy $\Delta H(0)/\Delta H(90)$ as a function of temperature. As with the temperature dependence of ΔH , there is negligible variation of the theoretical curves between 9.5 and 23.4 GHz. Here we note a discrepancy in the qualitative behavior below about 150°K . The decrease of $\Delta H(0)/\Delta H(90)$ with lowering T is also apparent from Elliston's data.¹⁴ This is particularly of interest since a basic feature of current theories²⁵ of linewidth in the critical region of uniaxial antiferromagnets, whether quasi- $2d$ or $3d$, seems to be that $\Delta H_{\parallel}/\Delta H_{\perp} \geq 2$, as has been observed^{11,26} in NiCl_2 and MnF_2 (\parallel and \perp refer to the field applied parallel and perpendicular, respectively, to the c axis of symmetry).

The above discrepancy may be due to temperature dependence of the exchange constants, a feature which has not been allowed for in the calculations. The fact¹⁵ that the crystal-field parameter D for Cr^{3+} in isomorphous NaInS_2 has the strongest temperature dependence of any known compound would seem to strengthen this argument. This temperature dependence has been ascribed to a change of relative interionic spacing occurring probably along the c direction, i. e., between the planar sheets. Assuming the c parameter to decrease with lowering temperature would result in an increase of J' . Then from Fig. 5 one concludes that $\Delta H(0)/\Delta H(90)$ should decrease as observed. To be specific, if $|J'/J|$ were to increase by a factor of 1.7 between 300 and 100°K —which is about the same as the observed¹⁵ decrease in the crystal-field parameter D —the decrease in $\Delta H(0)/\Delta H(90)$ would roughly be accounted for. At the same time, we would expect, also from Fig. 5, $\Delta H(90)$ to be about 8% lower at 100°K than its theoretical value shown in Fig. 2, which is in satisfactory agree-

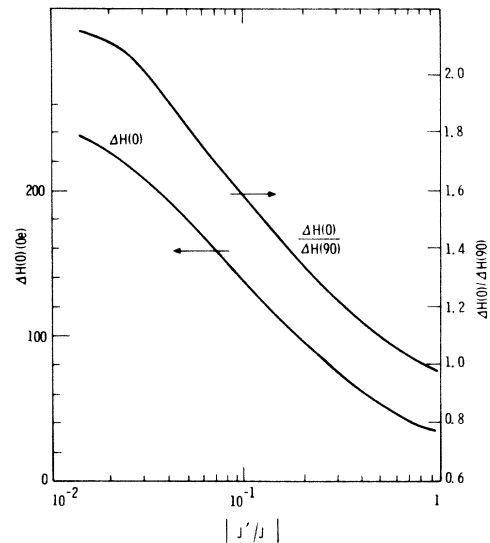


FIG. 5. Theoretical linewidth at $\theta = 0^\circ$ and anisotropy of ΔH vs $|J'/J|$. It should be borne in mind that Eq. (2), upon which these curves are based, is valid only for $|J'/J|$ sufficiently large that $\gamma\Delta H t_0 \ll 1$. This condition is satisfied for $|J'/J| = 10^{-1}$, but not for $|J'/J| = 10^{-2}$. When $\gamma\Delta H t_0 > 1$, the methods of I, which maintain a finite upper limit in the integral of Eq. (1), must be used.

ment with the solid curve. An x-ray investigation as a function of temperature to check for anisotropic lattice expansion would clearly be of value to test this point further.

V. SUMMARY AND CONCLUSIONS

The linewidth ΔH has been measured in the quasi- $2d$ compound NaCrS_2 , which has appreciable interplane coupling. Particular attention was paid to the angular dependence and variation with T in the high-temperature regime. The methods of Ref. 8 (I) were used to compute ΔH . Fairly good agreement was obtained, but not as good as obtained in I for the nearly ideal $2d$ compound K_2MnF_4 . The major successes of the theory are in predicting the anisotropy ratio $\Delta H(0)/\Delta H(90)$ at room temperature and in showing that interplane coupling removes the minimum at $\theta = \cos^{-1}(1/\sqrt{3}) \approx 55^\circ$, which is observed in K_2MnF_4 but not in NaCrS_2 . The ratio $\Delta H(0)/\Delta H(90)$ was shown to depend on t_0/τ_c , where $t_0 \approx c^2/D'$ is the characteristic time for crossover from $2d$ to $3d$ diffusion and $\tau_c \approx a^2/D$ is the characteristic time for initial decay of the correlations. The estimate from Eqs. (11) and (12) is $t_0/\tau_c \approx \frac{1}{2}(J/J')^2 = 18$ so that (Table I) we expect, and observe, $\Delta H(0) > \Delta H(90)$. Whether or not there is a minimum at 55° depends on $\omega_0 t_0$ (given that $t_0 \gg \tau_c$). We have $\omega_0 t_0 \approx 1$ at X band so that the calculation shows no minimum at 55° but does give a reduced

width at that angle. The observed room-temperature angular dependence agrees quite well with the calculation.

The line shape was Lorentzian at $\theta = 0^\circ$, in contrast to the situation in K_2MnF_4 , which we attribute to t_0 being sufficiently short ($\gamma\Delta H t_0 \ll 1$) in NaCrS_2 to remove the long-time anomalies in the line shape (1).

The linewidth increases continuously as T is lowered. This is expected for ferromagnetic coupling within the planes as in NaCrS_2 , regardless of the ultimate state of 3d ordering, and good agreement is obtained with theory. In this respect NaCrS_2 behaves more kosher than some other in-plane ferromagnets. NiCl_2 , K_2CuF_4 , and^{27,28} CrBr_3 all show ΔH initially to decrease as T is lowered from room temperature. A possible reason for this is that the broadening mechanism may be more nearly dipolar in NaCrS_2 than in the other compounds. The low-temperature anisotropy field¹² in K_2CuF_4 is three times greater than can be accounted for by the classical dipolar field, while both NiCl_2 and CrBr_3 have $\Delta H(0) = \Delta H(90)$ at high temperature, which would be hard to understand on the basis of purely dipolar coupling. The difference in resonance fields between $\theta = 0$ and 90° in NaCrS_2 is adequately given by dipolar effects, and the relatively small trigonal ligand field¹⁵ on the single Cr^{3+} ion in NaInS_2 also suggests that a single-ion anisotropy and anisotropic exchange may

be unimportant. One main conclusion of this paper is, in fact, that closer agreement between experiment and theory is found when the single-ion g values are isotropic to the third decimal place as for Mn^{2+} , as studied in I, and for Cr^{3+} in this compound.

Another material which should be commented on is CrCl_3 , which also has ferromagnetic planes antiferromagnetically coupled. The high-temperature linewidth²⁷ anisotropy is $\Delta H(0)/\Delta H(90) = 1.5$, in close agreement with that found in NaCrS_2 and in K_2MnF_4 . Also, the linewidth²⁷ does seem to increase as T is lowered below 240°K ; so CrCl_3 has features similar to those found here for NaCrS_2 .

The temperature dependence of $\Delta H(0)/\Delta H(90)$, which is observed to decrease below 150°K , cannot be explained within the context of the present theory for a fixed J'/J . This phenomenon, which is not observed in NiCl_2 , CrBr_3 , or CrCl_3 —all three of which show $\Delta H(0)/\Delta H(90)$ to increase with lowering T [temperature dependence of $\Delta H(0)/\Delta H(90)$ has not been reported for K_2CuF_4]¹²—may be related to a temperature dependence of J'/J .

In conclusion, NaCrS_2 has provided a good system in which to study the effects of interplane interactions J' and ferromagnetic in-plane coupling on linewidth in a quasi-2d system. The angular dependence of ΔH is particularly sensitive to J' and, with further refinements of the theory and clarification of the interactions, might provide a means for analyzing small J' in layer compounds.

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