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Narrowing effects in the ESR spectra of Gd in metals: Application to LaSb:Gd†

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The ESR spectra of Gd in metallic single crystals of LaSb exhibit appreciable variation in the ESR line shape upon changing the temperature from 1.7 to 300 K. At low temperatures, a completely resolved fine-structure splitting appropriate to Gd in a cubic crystalline field is observed. The fourth-order cubic-crystalline-field parameter is $b_4 = +32 \pm 2$ Oe. The increase of the temperature leads to significant narrowing effects with the result of a single anisotropic line at room temperature. A Korringa relaxation rate of $\Delta H_K/T = 0.19 \pm 0.03$ Oe/K was extracted from the thermal broadening of the collapsed spectrum. The thermal broadening of the $-1/2 \leftrightarrow +1/2$ fine-structure transition is considerably enhanced, however, with respect to this Korringa thermal broadening. All these features are in complete agreement with the predictions of the theory for exchange narrowing of the fine structure in metals. The ESR line shape was calculated using this theory. Comparison of the theoretical line shape with the one observed experimentally indicates the presence of an additional narrowing mechanism. This narrowing is due to Gd spin-spin interaction in LaSb. The line shape analysis yields an exchange-interaction parameter of 0.03 eV between the spin of Gd and that of the conduction electron. The same value for the exchange parameter is derived, independently, from the experimental Korringa thermal broadening.

I. INTRODUCTION

We report electron-spin-resonance investigations of Gd in LaSb metallic single crystals in a wide temperature range between 1.7 and 300 K. In the low-temperature region, completely resolved fine structure of Gd in a cubic crystalline field was observed, in agreement with previous publications about Gd in metallic lanthanum pnictides.[1,2] As the temperature is increased, exchange-narrowing effects in the ESR spectra begin to play a role. These narrowing effects manifest themselves by a complete collapse of the fine structure into a single anisotropic line at high temperatures. To the best of our knowledge, no report exists so far about "single-ion" narrowing effects in any intermetallic compound. In dilute alloys, it has been observed in Pd:Gd,[3] however, over a very limited temperature range. The temperature dependence of the ESR spectra can be interpreted in terms of the Plefka-Barnes theory.[4,5] This theory predicts a "single-ion" narrowing of the fine structure as a result of the exchange interaction between the spin of the Gd and that of the conduction electrons. The observation of narrowing effects over a wide temperature range enables us to check the theory for the nonbottleneck region in a critical manner.

One of the most interesting features of the Plefka-Barnes theory is associated with the large enhancement of the thermal broadening of the individual fine-structure transition with respect to the Korringa linewidth. It originates from "scattering-out"[6] relaxation of the individual fine-structure line into neighboring fine-structure transitions. This effect was observed experimentally in the present work and for the first time in metals. We found the thermal broadening of the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ fine-structure line to be by one order of magnitude larger than that of the collapsed spectrum. Such an observation in LaSb:Gd is possible because of the very wide temperature range over which narrowing effects occur. This is due to the very small Korringa rate (and thus, the "scattering-out" relaxation) with respect to the fine-structure splitting in this system.

In Sec. II of this paper, we shall describe the experimental results. Section III exhibits a line-shape analysis using the theory of Plefka-Barnes. We demonstrate that the calculated line shape deviates from the one observed experimentally, indicating an additional narrowing mechanism to exist in LaSb:Gd. The Gd spin-spin interaction is introduced phenomenologically into the theory (Sec. IV) to account for the above-mentioned deviation. Finally, a discussion is given in Sec. V. We mainly emphasize the properties which make LaSb:Gd most promising for a study of "single-ion" narrowing effects.

II. EXPERIMENTAL RESULTS AND ANALYSIS

The ESR experiments were performed mainly at 8-mm wavelength using a Varian spectrometer. Two single crystals of LaSb:Gd were used with Gd concentrations of 2000 and 250 ppm. The experimental results can be summarized as follows:

(i) Upon increasing the temperature, an appreciable narrowing occurs in the ESR spectra. Figure 1 shows the spectra in the [111] direction as measured for various temperatures. It is clearly seen that a complete collapse of the spectrum into a single line has taken place at 300 K.

(ii) The low-temperature results ($T \approx 4$ K) are very similar to those reported previously.[1] A completely resolved fine-structure spectrum was observed [Fig. 1(a)]. The angular variation of the individual lines is shown in Fig. 2 for a magnetic field rotating in the $(1\bar{1}0)$ plane. The solid lines in the same figure represent a theoretical fit using the spin Hamiltonian[7]

$$\mathcal{H} = \mu_B \mathbf{H} g \mathbf{S} + \tfrac{1}{60} b_4 (O_4^0 + 5 O_4^4), \qquad (1)$$

where b_4 is the fourth-order crystalline-field parameter for Gd. O_4^0 and O_4^4 are spin operators of fourth degree, μ_B is the Bohr magneton, and g is the Gd g value. The best fit in Fig. 2 yields the parameters

$$g = 1.990 \pm 0.003, \quad b_4 = +32 \pm 2 \text{ Oe} . \qquad (2)$$

The sign of b_4 was determined from the relative intensities of the different transitions of the resolved spectrum in Fig. 1(a).

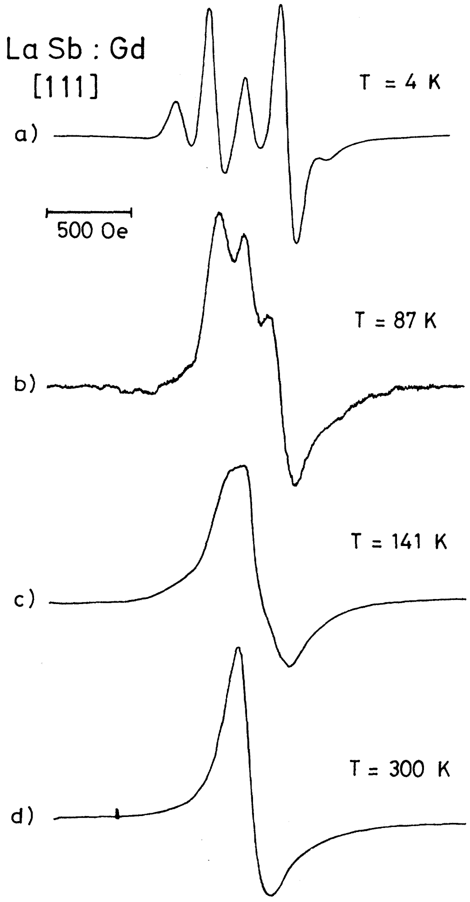

FIG. 1. ESR spectra of Gd (2000 ppm) in a single crystal of LaSb for various temperatures at a frequency $\nu = 34.7$ GHz. Spectra were measured for the magnetic field along the [111] direction.

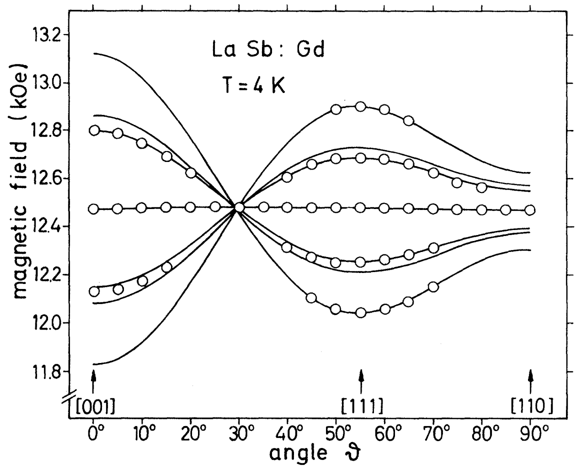

FIG. 2. Angular variations of the resonance fields of the seven $\Delta M = 1$ transitions for Gd in LaSb. Solid lines represent the calculated angular dependence using the parameters $b_4 = 32$ Oe, $g = 1.990$, and a frequency $\nu = 34.7$ GHz. Circles indicate experimental values.

(iii) At room temperature, a single line was observed for all orientations with, however, a significant angular variation in the linewidth (Fig. 3). The solid line in Fig. 3 can be fitted by the formula

$$\Delta H = A + B p^2(\vartheta) , \qquad (3)$$

where for the 2000-ppm sample, the values of A and B are equal to 95 and 130 Oe, respectively; $p(\vartheta)$ is given as

$$p(\vartheta) = 1 - 5(\sin^2\vartheta - \tfrac{3}{4}\sin^4\vartheta) . \qquad (4)$$

Here, ϑ is the angle between the external field and

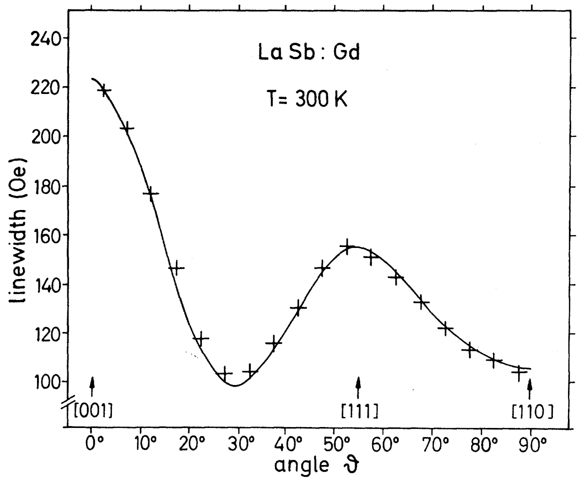

FIG. 3. Angular variation of the linewidth of the collapsed spectrum of LaSb : Gd (2000 ppm) at room temperature. Solid line represents a theoretical fit with relation (3) assuming $A = 95$ Oe and $B = 130$ Oe.

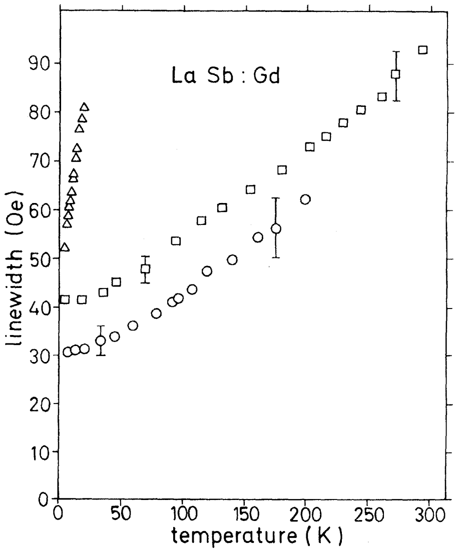

FIG. 4. Linewidth of Gd in LaSb as a function of temperature. Squares and circles represent measurements on the 2000- and 250-ppm samples, respectively. Measurements in these cases were performed for magnetic-field direction creating an angle of approximately 30° with respect to the [001] direction in the $(1\bar{1}0)$ plane of rotation. Triangles represent the linewidth of the $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ transition of the 2000-ppm sample. These measurements were carried out for the magnetic field along the [001] direction.

the [001] direction in the $(1\bar{1}0)$ plane of rotation. It should be mentioned that the shift in the field for resonance of the individual fine-structure line, with respect to that of the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ transition, is proportional to $p(\vartheta)$ in the first approximation.

(iv) The Korringa thermal broadening was measured when the external magnetic field creates an angle of approximately 30° with the [001] direction in the $(1\bar{1}0)$ plane of rotation. At this particular orientation, a single ESR line with a minimal linewidth is observed in the temperature range between 1.7 and 300 K (see also Fig. 2). Figure 4 exhibits the linewidth as a function of temperature. For the two samples (with 250 and 2000 ppm of Gd) at high temperatures, the same thermal broadening of 0.19 ± 0.03 Oe/K was observed. This indicates the absence of a bottleneck effect in the relaxation mechanism. Thus, this thermal broadening is actually the Korringa thermal broadening given by

$$\Delta H_K / T = (\pi k / g\mu_B) \langle J^2(q) \rangle \eta^2(E_F) \ , \qquad (5)$$

where $\eta(E_F)$ is the conduction-electrons' density of states for one spin direction at the Fermi level, and $\langle J^2(q) \rangle$ is the average over the Fermi surface of the wave-vector-dependent exchange parameter. Using $\eta(E_F) = 0.1$ states/(eV spin atom),[8] as well as $\Delta H_K / T = 0.19$ Oe/K, we found $\langle J^2(q) \rangle^{1/2} = 0.03$ eV. This exchange parameter corresponds, in the absence of appreciable wave vector q dependence, to a g shift of $|\Delta g| = 0.003$. The experimental g shift is $\Delta g = -0.002 \pm 0.003$. The negative sign is not understood yet.

(v) We have measured, also, the thermal broadening of the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ fine-structure line in the temperature range up to 20 K. For this measurement, the external magnetic field was parallel to the [001] direction. In this orientation the splitting is the largest, so that overlap and narrowing have the smallest influence on the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ transition. A linear increase of the linewidth with temperature of 2.0 ± 0.5 Oe/K was observed. The linewidth of the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ fine-structure line as a function of temperature is shown in Fig. 4.

III. THEORETICAL ANALYSIS

To analyze our experimental data, use was made of Plefka's theory.[4] According to this theory, the transverse dynamic susceptibility is given, in the nonbottleneck limit, by

$$\chi^{+}(\omega) \sim 1 - \omega \left[\sum_{M,M'} P_M (\Omega^{-1})_{M,M'} \right] \ , \qquad (6)$$

where M and M' are quantum numbers describing the various Zeeman states $(M, M' = -S, -S+1, \ldots, S-1)$, P_M are transition probabilities for transition from M to $M+1$ weighted by the Boltzmann factors and given as

$$P_M = C_M e^{M\hbar\omega/kT} \Big/ \sum_{M'} C_{M'} e^{M'\hbar\omega/kT} \ . \qquad (7)$$

C_M, therefore, is given by $C_M = S(S+1) - M(M+1)$. The elements $\Omega_{M,M'}$ of the transition matrix for temperatures kT large compared to $\hbar\omega$, are expressed by the formula

$$\Omega_{M,M'} = (\hbar\omega/g\mu_B - H - H_M)\delta_{M,M'} - i\Delta H_{\mathrm{res}}\delta_{M,M'}$$
$$- i\tfrac{1}{2}\Delta H_K \, C_{M'}(2\delta_{M,M'} - \delta_{M,M'+1} - \delta_{M,M'-1}) \ , \qquad (8)$$

where $\omega/2\pi$ is the microwave frequency, H the variable external magnetic field, H_M the field for resonance of the fine-structure line of the $M \rightarrow M+1$ transition (Fig. 2), and ΔH_{res} the temperature-independent residual linewidth of the various fine-structure lines. The parameter ΔH_{res} was introduced into the theory phenomenologically.

At this stage it is instructive to consider two limiting cases:

(i) For a completely resolved spectrum, the theory of Plefka predicts a width for the individual fine-structure line of the $M \rightarrow M+1$ transition to be[4]

$$\Delta H(M \rightarrow M+1) = \Delta H_{\mathrm{res}} + C_M \Delta H_K \ . \qquad (9)$$

The Korringa linewidth ΔH_K is proportional to the temperature. Thus, the thermal broadening of the

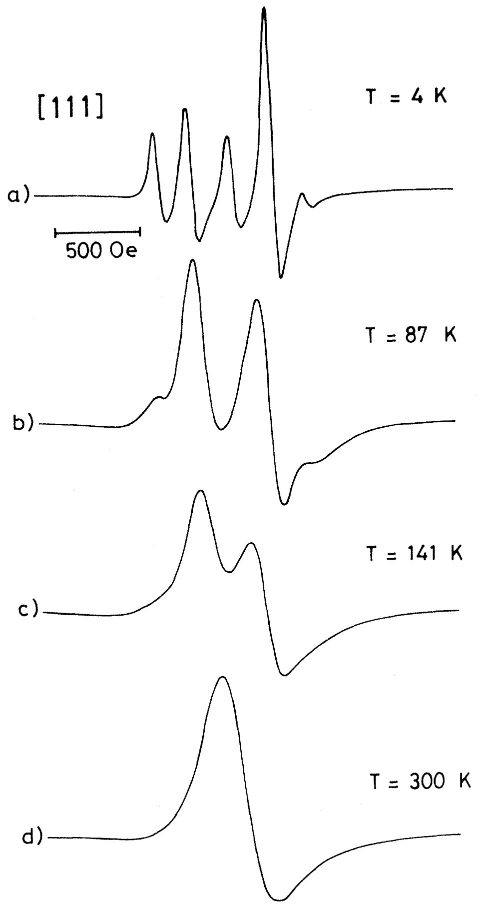

FIG. 5. Calculated ESR spectra for [111] direction of Gd in LaSb for different temperatures considering "single-ion" narrowing only.

individual fine-structure transition should be enhanced by a factor C_M over the value of the Korringa thermal broadening. For $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ transition, one expects, therefore, an enhancement by a factor of 16, i.e., a thermal broadening of approximately 3 Oe/K.

(ii) Case (ii) deals with the linewidth of the unresolved spectrum in the extreme narrowing region. In this limit, the theory of Plefka predicts when applied to the spin Hamiltonian (1),

$$\Delta H(\vartheta) = \Delta H_{\text{res}} + \Delta H_K + \tfrac{44}{3}\, p^2(\vartheta) b_4^2 / \Delta H_K \ , \tag{10}$$

where $\Delta H(\vartheta)$ is the resonance width as measured for a magnetic-field orientation with respect to the [001] direction. Equation (10) indicates that even in the narrowing region the unresolved linewidth might be angular dependent.

These two cases are extremely interesting features of the theory. In Sec. V it will be shown that indeed, the experiment performed on LaSb:Gd supports the theory.

Using (6)–(8), we have calculated the function $[\text{Re}\,\chi^+(\omega) - \text{Im}\chi^+(\omega)]$. The actual theoretical line shape is given by a computer plot of the first derivative of this function with respect to the external magnetic field.

Figure 5 shows calculated spectra for various temperatures assuming the parameters $\Delta H_{\text{res}} = 35$ Oe, $\Delta H_K / T = 0.19$ Oe/K, and H_M as given by Fig. 2. Although the general features of the calculated line shapes are similar to those observed experimentally (see Fig. 1), some deviations exist. We attribute them to spin-spin narrowing effects, which will be discussed in the Sec. IV.

IV. SPIN-SPIN INTERACTION EFFECTS

A detailed comparison between the theoretical spectra (Fig. 5) and the experimental ones (Fig. 1) reveals the following differences: (i) In the theoretical spectrum, the narrowing occurs at slightly higher temperatures than in experiment. (ii) The transition $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ does not appear in the theoretical spectra in the intermediate temperature range [Fig. 5(b) and Fig. 5(c)]. It appears, however, in the experiment [Fig. 1(b) and Fig. 1(c)]. (iii) The experimental linewidth of the single line at room temperature is smaller than the calculated one.

We shall demonstrate in this section that these discrepancies between theory and experiment can be overcome by introducing spin-spin exchange interaction between the Gd ions. Indeed, previous publication of the fine-structure splitting in LaSb:Gd clearly indicates the existence of such a narrowing mechanism.[1]

Unfortunately, no theoretical calculation which takes spin-spin interaction into consideration exists at present. In the absence of such a theory, we shall introduce the spin-spin interaction in a phenomenological way. This was done by adding to the matrix element $\Omega_{M,M'}$ in (8) a further term $\Omega^{\text{ex}}_{M,M'}$ describing the spin-spin interaction

$$\Omega^{\text{ex}}_{M,M'} = i\,\frac{H_{\text{ex}}}{P_M}(1 - \delta_{M,M'}) - i\,\frac{6H_{\text{ex}}}{P_M}\,\delta_{M,M'} \ , \tag{11}$$

where H_{ex} is the exchange-field parameter in the sense of Ref. 9. Two principles are fulfilled by this modification of $\Omega_{M,M'}$. Firstly, $P_M\,\text{Im}\Omega_{M,M'}$ are the elements of a negative-definite symmetric matrix. This guarantees a positive energy absorption. Secondly, as the total spin commutes with the exchange Hamiltonian, the relation $\sum_{M'} \Omega^{\text{ex}}_{M,M'} = 0$ must hold. Since these two requirements are satisfied, we have some confidence that expression (11) describes the main effects of the spin-spin interaction.

Our calculations using one single exchange field H_{ex} show the expected narrowing effect upon increasing H_{ex}. But in the intermediate temperature range around 100 K where the theoretical line

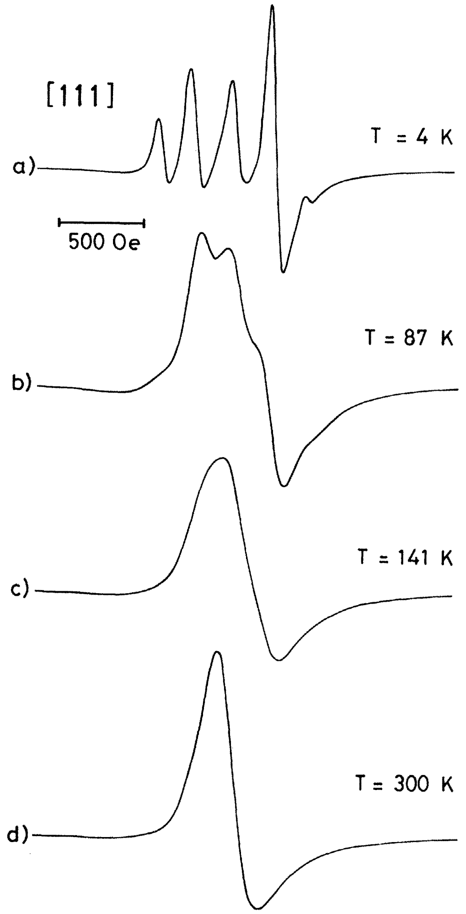

FIG. 6. Calculated ESR spectra for [111] direction of Gd in LaSb for different temperatures considering both "single-ion" and spin-spin narrowing.

shape does not exhibit the $-\frac{1}{2}\leftrightarrow+\frac{1}{2}$ transition for $H_{ex}=0$ [Fig. 5(b)], an increase of H_{ex} leads to a complete collapse of the spectrum into one single line. Thus, we were not able to fit observed spectra as shown, for example, in Fig. 1(b) by using one single exchange field H_{ex}. Because of the random distribution of the Gd ions, however, it is realistic to assume a distribution of H_{ex}. In this case, we reach a good agreement between theoretical spectra (Fig. 6) and experiment (Fig. 1). The calculation of the spectra of Fig. 6 is based upon an exchange-field distribution of slightly modified Lorenzian character with a maximum at $H_{ex}=0$. The mean exchange field amounts to about 300 Oe; the distribution function was cut off at 1500 Oe.

V. DISCUSSION

As we mentioned above, "single-ion" narrowing effects have been observed already in dilute Pd:Gd alloys.[3] The results exhibit features predicted by Plefka[4] and Barnes,[5] but the narrowing effects occur in a small temperature range from 1.4 to 5.2 K. Furthermore, the occurrence of clusters and long-range spin-spin interaction may modify the spectrum completely, as demonstrated above.

The great advantage of the LaSb:Gd system is associated with the relative low density of states: $\eta(E_F)\approx 0.1$ states/(eV spin atom).[8] This small density of states yields a small Korringa relaxation which, together with the relatively large fine-structure splitting, is responsible for the observation of "single-ion" narrowing effects over a wide temperature range of approximately 300 K! It is this extraordinary property which enables one to examine the theory in detail.

Theoretically, the ESR spectra—in the presence of "single-ion" exchange narrowing—should exhibit two unique features: (i) The thermal broadening of the $M\leftrightarrow M+1$ fine-structure transition should exceed the Korringa thermal broadening by a factor of $S(S+1)-M(M+1)$, and (ii) The collapsed spectrum at high temperatures should reveal angular variation proportional to $p^2(\vartheta)$, as shown by Eq. (10).

Experimentally, the $-\frac{1}{2}\leftrightarrow+\frac{1}{2}$ transition exhibits a thermal broadening of 2.0 ± 0.5 Oe/K. This value is by one order of magnitude larger than the Korringa thermal broadening of 0.19 ± 0.03 Oe/K, which is in satisfying agreement with the theory.

Concerning the angular variation of the collapsed spectrum, Fig. 3 shows that behavior at 300 K. This experimental angular variation is proportional to $p^2(\vartheta)$ according to (3). Quantitative fitting can be obtained by comparing (3) with (10). The requirement $A=\Delta H_{res}+\Delta H_K$ is easily satisfied, but the experimental value of B is smaller by a factor of 2.0 than the theoretical one of $44b_4^2/3\Delta H_K$. If, however, we take spin-spin exchange interaction into consideration, a complete agreement between experiment and calculation is obtained.

Finally, a few words concerning relation (10). This relation is extremely interesting, as it predicts a possible contribution to the linewidth upon decreasing temperature at low temperatures (i.e., small ΔH_K). This is associated with crystalline-field narrowing and was pointed out already for hexagonal systems.[10] It might lead to possible errors in the determination of $\Delta H_K/T$, especially in polycrystalline samples if the third term in (10) cannot be neglected. A decrease of the linewidth with increasing temperature at low temperatures has been observed in the ESR of many dilute alloys. This has often been interpreted as an "ordering effect," whereas, in certain cases, it might actually be associated with the third term in (10). Thus, one should be very careful in estimating the thermal broadening from low-temperature data. In our case, the extraction of the Korringa rate above was made in a magnetic-field orientation in such a way that the function $p(\vartheta)$ exhibits a minimum. In this particular orientation, our estimate indicates that the third term in (10) can be neglected above 20 K.

In conclusion, we have observed the narrowing of the resolved fine structure at low temperatures to a completely collapsed spectrum at room temperature. This behavior is consistent with the theoretical predictions for exchange interaction in dilute magnetic alloys.

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