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Moment Reduction in Magnetically Ordered Samarium Intermetallics

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The influence of cubic crystalline fields on the magnetic moment of the Sm^{3+} ion is calculated, with inclusion of the mixing of higher multiplet levels into the ground multiplet. It is shown that the magnetic moment residing on the samarium, which in a number of intermetallics is observed to be substantially reduced with respect to the free-ion value, can easily be explained on this basis. From a comparison with the corresponding gadolinium compounds it is found that the moment reduction by conduction-electron polarization is less important.

I. INTRODUCTION

In metallic rare-earth systems in the magnetically ordered phase, the major contribution to the rare-earth sublattice magnetization is due to the localized moments residing on the rare earths themselves. These moments are given by the expectation value of $L_z + 2S_z$ of the lowest level of the ground J multiplet, i.e., $\mu = -\langle L_z + 2S_z \rangle \mu_B$. In the absence of crystal fields this reduces to $\mu = gJ\mu_B$, where g is the Landé g value. An additional, but smaller, contribution to the saturation moment is usually assumed to originate from the conduction electrons polarized by the rare-earth spins through s-f exchange interaction. In the formula[1] $\Delta\mu = -(3Z/4E_F)\mathcal{J}(0)\langle S_z \rangle \mu_B$, where $\mathcal{J}(0)$ is the spatially uniform part of the exchange integral, Z is the average number of conduction electrons per atom and E_F is the Fermi energy. For the first-half of the series of tripositive rare-earth ions, where $J = L - S$, the conduction-electron contribution therefore will reduce the net saturation moment for a positive $\mathcal{J}(0)$ and will enhance the moment for a negative $\mathcal{J}(0)$. On the other hand, for the second-half of the series, where $J = L + S$, and for Gd^{3+}, which has $J = S$, the conduction-electron effects are reversed.

These effects have recently been discussed by Stewart.[2] In particular, taking $\mathcal{J}(0)$ positive, he pointed out that in the case of Sm^{3+}, an L-S ion with a small g value ($g = \frac{2}{7}$) and thus a low magnetic moment ($\mu = 0.71\,\mu_B$) associated with a high spin moment, the reduction might be appreciable. In this way he accounted for the saturation moment of about $0.2\,\mu_B$/atom observed for samarium metal.[3] It is well known, however, that crystal fields, which essentially have been ignored by Stewart, also provide a mechanism that reduces the saturation moment of rare-earth ions. Indeed, there exists a vast body of experimental evidence[4] of the presence of crystal fields in rare-earth metals as well as their intermetallic compounds, so that there is absolutely no basis to leave them out of consideration. It is the purpose of the present paper to study the effects of crystal fields on the saturation moment of Sm^{3+}. By cubic crystal fields the lowest multiplet level of Sm^{3+} ($J = \frac{5}{2}$) is split into a doublet Γ_7 and a quartet Γ_8 with, in vanishing exchange field along the [001] axis, magnetic moments of $0.238\,\mu_B$ and $0.524\,\mu_B$, respectively.[5] The simple approach of confining oneself to a crystal-field splitting within the ground multiplet only therefore seems to be adequate to account for the moment reduction (see Table I).

TABLE I. Curie temperatures, low-temperature saturation moments, and lattice parameters of some samarium and gadolinium cubic Laves-phase compounds.

Compound	T_C (K)	$\lvert\mu\rvert$ (μ_B)	a (Å)	Ref.
$SmAl_2$	120	0.2	7.945	a
$SmIr_2$	37	0.2	⋯	b
$SmRh_2$	22	0.53	7.537	c
$SmNi_2$	21	0.25	7.218	d
$SmPt_2$	6	0.19	7.662	e
$GdAl_2$	171	7.0	7.900	f
$GdIr_2$	90	6.83	7.550	b
$GdRh_2$	75	6.80	7.517	c
$GdNi_2$	85	7.1	7.193	d
$GdPt_2$	37	6.77	7.636	c

[a] Reference 6.

[b] R. M. Bozorth, B. T. Matthias, H. Suhl, E. Corenzwit, and D. D. Davis, Phys. Rev. 115, 1595 (1959).

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However, crystal-field-induced mixing of higher multiplet levels into the ground multiplet, in particular that of the $J=\frac{7}{2}$ at a distance of only about 1500 K, is expected to be substantial. Indeed, the anomalous signs of the Al^{27} Knight shift in SmAl_2 and the Sn^{119} Knight shift in SmSn_3,[6] as well as the change of the direction of magnetization in SmFe_2 with temperature,[7] could only be explained with inclusion of this mixing. It will be shown below that the mixing reduces the moment further than expected from crystal fields acting within the $J=\frac{5}{2}$ only. The reduction may even be so drastic that the magnetic moment reverses its sign relative to the spin. From a subsequent comparison with experimental data for the cubic Laves-phase compounds RX_2 (R = rare earth and X = Al, Ir, Rh, Pt, Ni), it appears that also in the case of Sm compounds the crystal-field-induced reduction is stronger than the effect of conduction-electron polarization.

II. CALCULATIONS AND DISCUSSION

The expectation values of moment and spin of the ground level of Sm^{3+} in the presence of crystalline fields and a molecular field are calculated as follows. In view of the rather large ordering temperatures observed for some Sm intermetallics, the calculations have been carried out for various values of the molecular field. The energy levels of the Sm^{3+} ion are obtained by diagonalizing the Hamiltonian

$$\mathcal{H}=\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}+\mathcal{H}_c+2\mu_B\vec{\mathrm{H}}_{\mathrm{ex}}\cdot\vec{\mathrm{S}}\ . \tag{1}$$

For the spin-orbit coupling parameter λ the value $\lambda/k_B=410$ K has been used. The molecular field H_{ex} has been chosen to be parallel to the [001], [011], or [111] direction. The crystal-field Hamiltonian $\mathcal{H}_c$ is given by

$$\mathcal{H}_c=A_4\sum_i(f_{40}+5f_{44})+A_6\sum_i(f_{60}-21f_{64})\ , \tag{2}$$

where the z axis has been taken parallel to one of the $\langle 001\rangle$ cubic axes, and the summation runs over all the $4f$ electrons. The calculation of the matrix elements of the functions f_{k_q} has been carried out as described in our previous papers.[6,7] In the diagonalization we have included all diagonal as well as off-diagonal elements within and between $J=\frac{5}{2}$ and the first two excited states $J=\frac{7}{2}$ and $\frac{9}{2}$. Then, the expectation values of L_z+2S_z and S_z have been calculated for various values of the parameters $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$, and H_{ex}, with H_{ex} parallel to [001], [011], or [111]. Again, all matrix elements within the lowest three multiplet levels have been included.[6]

The case of vanishing H_{ex}, Fig. 1, is appropriate for comparison with compounds with low Curie temperature T_C. The $J=\frac{5}{2}$ multiplet is split by the cubic crystal field into a doublet Γ_7 and a quartet Γ_8. The doublet Γ_7 is lowest for the combinations of crystal-field parameters at the right-hand side of the dashed line in Fig. 1, whereas the quartet Γ_8 is the ground state in the left-hand part. The dashed line thus indicates those cases for which Γ_7 and Γ_8 accidentally coincide. Figure 1 gives $\langle L_z+2S_z\rangle$ and $\langle S_z\rangle$ for the level which in a small exchange field along the positive z direction will be the ground level, i.e., for that sublevel of Γ_7 or Γ_8, dependent on which is lowest, which has the largest negative $\langle S_z\rangle$. Figure 1 has been calculated for $\vec{\mathrm{H}}_{\mathrm{ex}}\parallel[001]$. The expectation values $\langle L_z+2S_z\rangle$ and $\langle S_z\rangle$ for the part with Γ_7 lowest appear, however, to be independent of the orientation of H_{ex}.

Figures 2 and 3 give the development of $\langle L_z+2S_z\rangle$ with increasing H_{ex}. The energy levels are now nondegenerate, except for accidental degeneracy, which for the lowest levels is indicated by dashed lines. With the exchange field pointing in the positive z direction, as in Fig. 1, $\langle S_z\rangle$ of the lowest

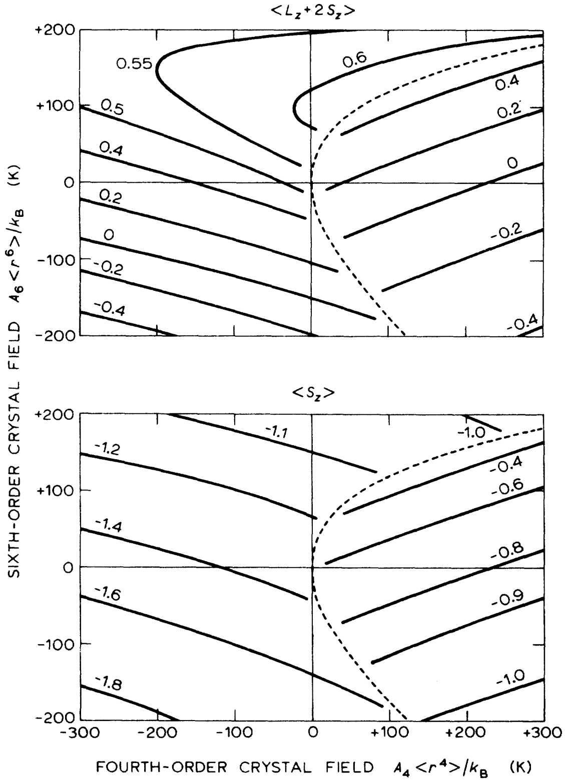

FIG. 1. Diagrammatical representation of $\langle L_z+2S_z\rangle$ and $\langle S_z\rangle$ of the ground level of Sm^{3+} in cubic crystal fields in the limiting case $\mu_BH_{\mathrm{ex}}/k_B=0$ K along [001]. The dashed curves are combinations of the crystal-field parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ for which the Γ_7 and Γ_8 originating from $J=\frac{5}{2}$ are accidentally degenerate.

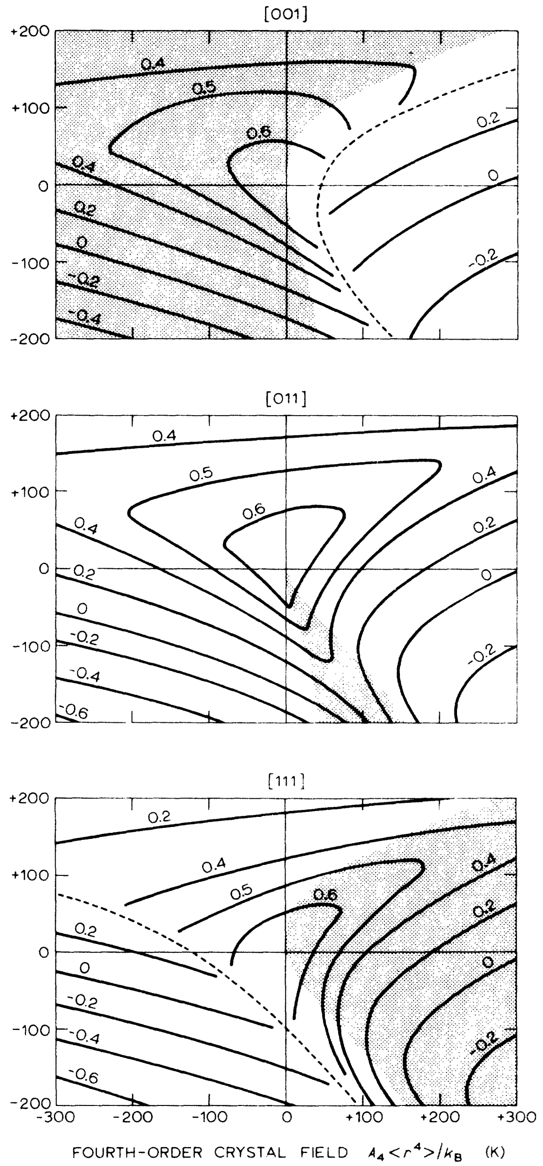

FIG. 2. Diagrammatical representation of $\langle L_z+2S_z\rangle$ of the ground level of Sm^{3+} in cubic crystal fields. The positive z axis is along H_{ex}. The exchange field $\mu_B H_{ex}/k_B=20$ K is directed in the [001], [011], and [111] directions, respectively. In the origin $\langle L_z+2S_z\rangle$ reaches its maximum value of 0.666. The dashed curves represent accidental degeneracy of the lowest levels. The shaded regions indicate cases where the easy magnetization and exchange field direction coincide near $T=0$ K, if the anisotropy were exclusively crystal-field anisotropy of the Sm^{3+} ion.

of the exchange split levels is of course *negative*. From the diagrams it is seen that $\langle L_z+2S_z\rangle$ can be either positive or negative. The former case, corresponding to $\langle L_z+2S_z\rangle$ and $\langle S_z\rangle$ being antiparallel, is the situation normally occurring in the tripositive rare earths out of the first-half of the series. The cases in which $\langle L_z+2S_z\rangle$ is negative, i.e., $\langle L_z+2S_z\rangle$ and $\langle S_z\rangle$ are parallel, are, however, similar to the situation of rare earths out of the second-half of the series, including Gd^{3+}. Loosely speaking, we might say that in these cases Sm^{3+} behaves as if it were an $L+S$ ion.

The easy axis of magnetization is of course determined by the well-known sources of anisotropy, including dipolar fields. When the anisotropy arises from single-ion anisotropy, the easy axis is given by the direction for which the free energy $-k_B T\ln Z$, with Z the state sum over the crystal-

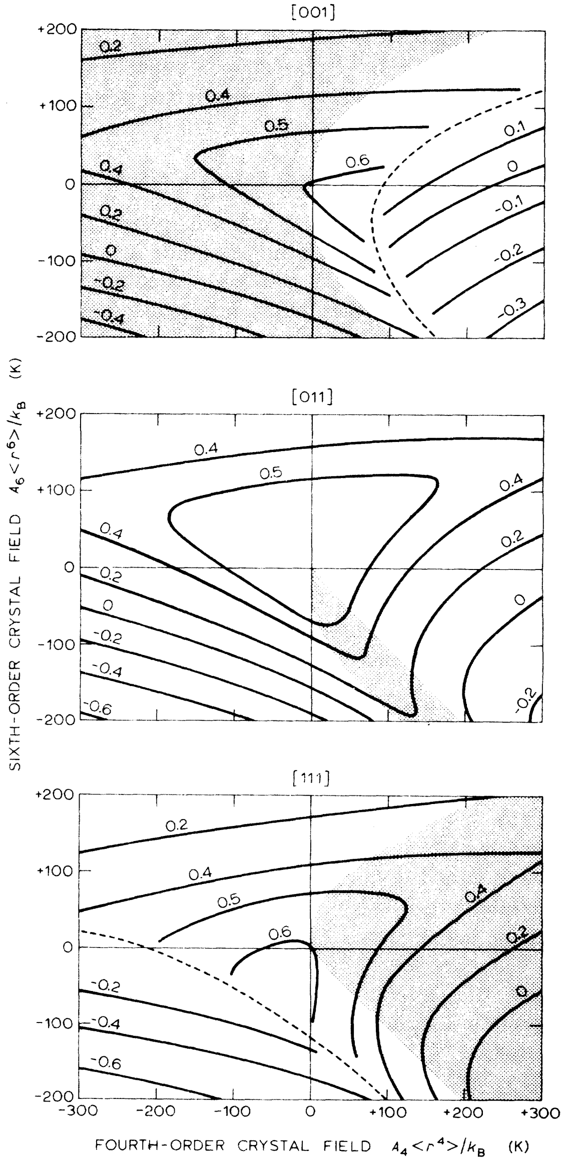

FIG. 3. Same as Fig. 2, except $\mu_B H_{ex}/k_B=50$ K. In the origin, $\langle L_z+2S_z\rangle=0.602$.

field levels, is a minimum.[7] For low H_{ex} at $T=0$ K this appears to imply that in the case with Γ_8 as lowest state the easy axis tends to be aligned along [001], so that Fig. 1 is pertinent in most practical cases. For higher values of H_{ex}, Figs. 2 and 3, the easy axis, as preferred by the single-ion crystal-field anisotropy at $T=0$ K, has been indicated by shading the crystal-field combinations in the relevant diagram.

We will now compare the above results with experimental data on Sm compounds of the cubic Laves-phase structure. These compounds are relatively easy to prepare in single-phase condition so that interference of magnetic impurity phases can be avoided. Further they order ferromagnetically at low temperatures, which makes possible the determination of the Sm^{3+} moments from magnetization measurements. We have gathered the experimental data of Sm compounds in Table I together with their Gd counterparts. All these data were taken from literature except those of $SmPt_2$. For the latter, in which T_C is rather low, we repeated the determination of the magnetic moment at 2 K in somewhat higher magnetic fields (up to 30 kG). Even at 30 kG the magnetization was observed to be still field dependent. The value listed in Table I, attained at 30 kG, comes quite close to the extrapolated moment derived from measurements in fields up to 18 kG by Crangle and Ross.[8] It is seen from the table that for most of the Sm compounds the ground-state moment differs appreciably from the free-ion value $0.71\mu_B$.

It will first be argued that this reduction cannot be attributed to conduction-electron polarization. In the absence of crystal fields, Sm^{3+} is a normal L-S state ion, so that a conduction-electron polarization which reduces the moment in the Gd compound is expected to enhance the moment in the corresponding Sm compound, and vice versa. In fact, since for the ground multiplet of Sm, $\langle S_z\rangle_{Sm}/\langle S_z\rangle_{Gd}=-\frac{25}{49}$, an excess moment of $0.2\mu_B$ for Gd implies a reduction by $0.1\mu_B$ for Sm. Inspection of the data in Table I shows that a moment *enhancement* of this order should have been observed on the basis of conduction-electron polarization for $SmIr_2$, $SmRh_2$, and $SmPt_2$, in obvious disaccord with experiment. Also, in the cases of $SmAl_2$ and $SmNi_2$ conduction-electron polarization effects cannot bridge the gap between the observed moment and the free-ion value. On the other hand, it has become clear from the calculations presented above (Figs. 1–3) that crystal fields of reasonable magnitude are able to account for the reduction. It is unfortunate that for none of the Sm compounds the precise values of the crystal-field parameters and the exchange field are known. In $SmAl_2$ the direction of easy magnetization is along [111], with $\langle S_z\rangle$ antiparallel to $\langle L_z+2S_z\rangle$.[9] In comparing with the diagrams (for $SmAl_2$, $\mu_B H_{ex}/k_B\approx 50$ K), the experimental moment should therefore be taken as positive ($+0.2\mu_B$/atom). In a previous paper, containing an analysis of the susceptibility and the Al Knight shift in $SmAl_2$ in the *paramagnetic* region, possible sets of crystal-field parameters could be derived (Fig. 5 of Ref. 6). Taking now everything together, it appears that crystal-field parameters of the order of $+100$ and -100 K for $A_4\langle r^4\rangle/k_B$ and $A_6\langle r^6\rangle/k_B$, respectively, are consistent with (a) the data in the paramagnetic region, (b) the observed ground-state moment in the ferromagnetic region, and (c) the direction of the easy magnetization. It seems paradoxical that in the paramagnetic region the (statistically averaged) expectation values of S_z and L_z+2S_z are observed to be parallel, whereas experiments performed in the ferromagnetic regime showed the expectation values of S_z and L_z+2S_z to be antiparallel. It is noted that this apparent paradox of the Sm^{3+} ion is explained by the dependence of the magnetic moment on H_{ex} (compare, for instance, Figs. 1 and 3).

We finally note that conduction-electron polarization effects in Sm^{3+}, already small in themselves are also affected by crystal fields, both in magnitude and sign. Within a multiplet of constant J, the conduction-electron polarization effects, proportional to $\langle S_z\rangle$, will be reduced by crystal fields at the same rate as the moment. As discussed above, however, in the case of Sm^{3+}, $\langle S_z\rangle$, which is no longer directly proportional to $\langle L_z+2S_z\rangle$, may in addition adopt a reversed sign, thereby changing the sign of the conduction-electron polarization on the magnetic moment as well. An analysis of conduction-electron polarization effects in samarium materials therefore makes sense only in conjunction with a crystal-field analysis with inclusion of J mixing, or an experimental determination of $\langle S_z\rangle$.

III. CONCLUDING REMARKS

Above it has been shown that the large moment reduction in Sm materials is explained by the occurrence of crystal fields. An interesting aspect which emerges from the results shown in Figs. 1–3, is that in some respects Sm^{3+} may behave as an $L+S$ ion in the magnetically ordered state, and that this behavior can persist for appropriate crystal fields even in the presence of large exchange fields. This feature bears important consequences for compounds in which the Sm sublattice is coupled to the sublattice of a 3*d* element, such as Fe, Co, or Ni. It is well known that in such compounds the 3*d* spins are usually coupled antiparallel to the rare-earth spins, which leads to large values of the saturation magnetization in the case of $L-S$ rare-earth ions, and, on the other hand, a partial cancellation of the two sublattice magnetizations in the case of $L+S$ ions. It is very well possible that the low values of the saturation magnetization of compounds such as $SmCo_5$, Sm_2Co_{17}, $SmFe_2$, and Sm_2Fe_{17}, which are inferior to those observed for the corresponding Y compounds, are largely caused by a crystal-field induced sign reversal of $\langle S_z \rangle$ relative to $\langle L_z + 2S_z \rangle$ of the Sm^{3+} ions.

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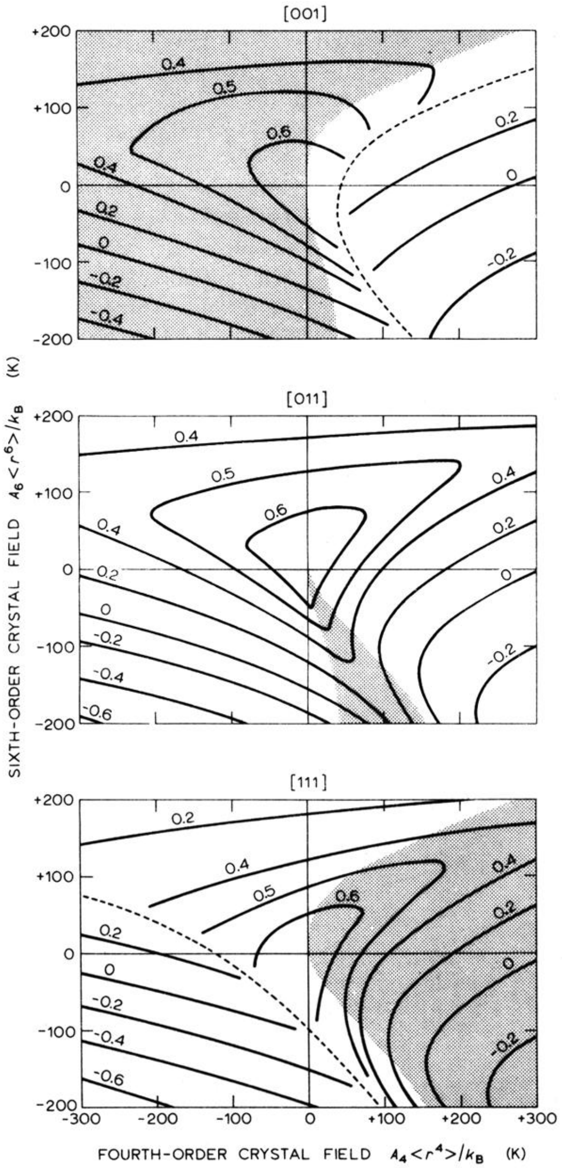

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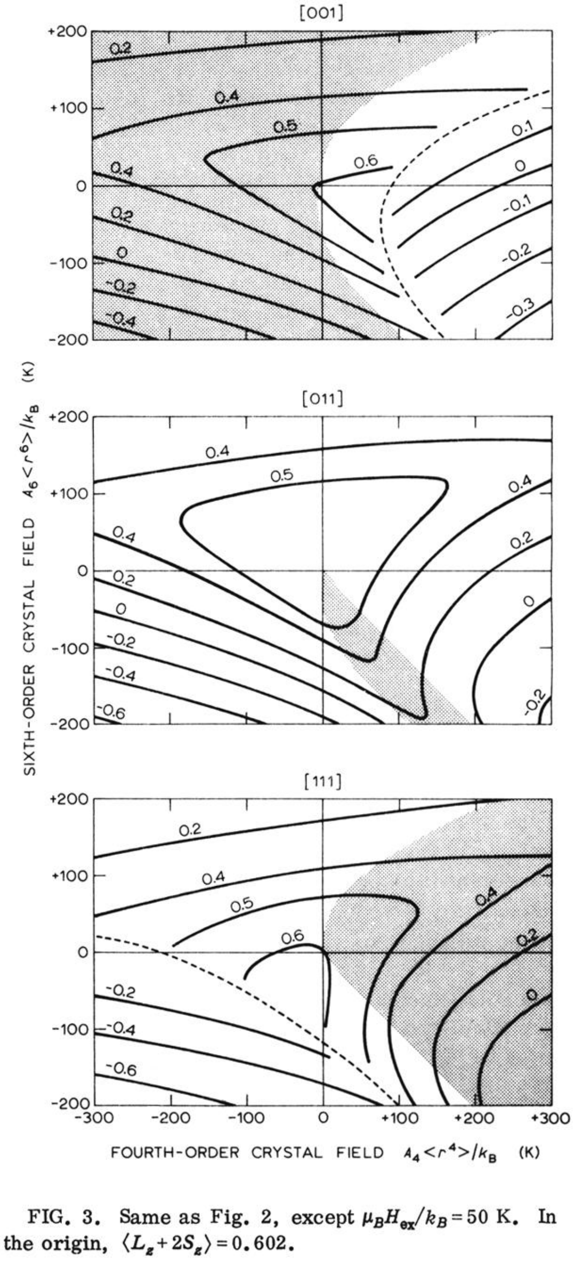

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