Magnetization measurements of reentrant ferromagnetic superconductors: The pseudoternary system $(Er_{1-x}Ho_x)Rh_4B_4$

H. Adrian, K. Müller, and G. Saemann-Ischenko
Physikalisches Institut der Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany

(Received 9 May 1980)

The magnetization of cylindrical samples of $Er_{1-x}Ho_xRh_4B_4$ has been measured in the temperature range from 1.4 K to $T_{c1}(x)$. The low-temperature parts of the bell-shaped $H_{c2}(T)$ curves show an increasingly pronounced anomaly with increasing T_{c2}. The low-temperature magnetization curves and the observed behavior of H_{c1} vs T suggests a transition from type-II to type-I superconductivity in the vicinity of T_{c2}. The normal-state magnetic susceptibility follows a Curie-Weiss law with a Curie temperature significantly below T_{c2} for $x \geq 0.40$. $(dH_{c2}/dT)/_{T=T_{c1}}$ is found to be constant within experimental error for $x \leq 0.60$, but about a factor of 3 smaller for $x = 0.70$.

I. INTRODUCTION

The discovery of superconductivity in several ternary compound systems containing large amounts of magnetic ions at regular lattice sites[1–4] has stimulated many experimental[5–14] and theoretical[15–36] studies on the coexistence of superconductivity and ferromagnetic order. In particular, the phenomenon of reentrant superconductivity observed in the ternary rare-earth compounds $HoMo_6S_8$ (Ref. 37) and $ErRh_4B_4$ (Ref. 38) and the possibility of gradually changing the strength of the magnetic interaction by using pseudoternary systems[5,39–44] offer a unique opportunity to investigate the interplay between superconductivity and magnetism. Reentrant superconductors become superconducting at an upper critical temperature T_{c1} and return to the normal state at a lower critical temperature $T_{c2} < T_{c1}$. Several theories predict a variety of superconducting properties, e.g., the shape of the H_{c2} vs T curves,[17,21,31] a change from type-II behavior to type-I behavior near T_{c2},[21] or the slope of the upper critical field near T_{c1},[33] which should be tested experimentally.

We report here results of magnetization measurements of the pseudoternary system $Er_{1-x}Ho_xRh_4B_4$ in the temperature range from 1.4 K to T_{c1} for $x = 0$, 0.15, 0.20, 0.27, 0.40, 0.50, 0.60, and 0.70.

II. EXPERIMENTAL

The samples were prepared by arc melting the appropriate amounts of the high-purity elements in zircon-gettered argon atmosphere. After remelting several times, the samples were sealed in tantalum tubes and annealed at 1050 °C for 2 weeks. Subsequently the temperature was slowly reduced ($\approx 10\,°C/20$ min) to room temperature to avoid cracks. From the ingots cylinders of about 1-mm diameter and 6-mm length were machined by an ultrasonic technique. The magnetization measurements were carried out with a conventional integrating setup using concentric pickup coils. The temperature was measured with a carbon-glass resistor. The temperature stability was better than 10 mK. The samples were mounted on a separate sample holder and could be taken out of the pickup coils at low temperature. Besides balancing the pickup system at the proper temperature, this made it possible to raise the sample temperature above T_{c1} to drive out trapped flux between different measurements. In order to reduce geometry effects as much as possible we used cylindrical samples which had demagnetization factors N between 0.06 and 0.12. The measured magnetization curves were corrected for the remaining demagnetization effects by calculating the effective external magnetic field $H_{ext,c} = H_{ext} - MN$, where M is the measured magnetization. This correction leads to an increase (decrease) of the magnetic field where the magnetization is negative (positive). Further on the subscript c is omitted. In the low-field region ($H_{ext} < H_{c1}$) the slope of the magnetization was $(dM/dH_{ext})|_{H_{ext}<H_{c1}} = -1 \pm 0.08$. The small deviations from the theoretically expected value were attributed to uncertainties in the determination of sample diameters. Therefore it is reasonable to multiply the measured magnetization by a constant factor to yield $(dM/dH_{ext})|_{H_{ext}<H_{c1}} = -1$ for comparison.

III. RESULTS AND DISCUSSION

H_{c1} was determined as the field, where M deviates from the straight line $M=-H_{\text{ext}}$ when the field is increased from zero, H_{c2} as the field, where the magnetization curve becomes hysteretic when the field is decreased from high values. As a typical example Fig. 1 shows the magnetization curves of $Er_{0.73}Ho_{0.27}Rh_4B_4$ at 6.86, 4.64, and 1.43 K (indicated by arrows). Generally three distinct field regions can be identified for temperatures $T_{c2} < T < T_{c1}$: If the external magnetic field is increased from zero, the samples are at first in the Meissner state, $M=-H$. As no magnetic field enters, the samples behave like a nonmagnetic superconductor. With further increasing field the samples enter the mixed state and the total magnetization is the sum of a positive paramagnetic part due to the rare-earth ions and a negative part due to superconductivity. In high fields superconductivity is completely destroyed and the magnetization is that of a usual paramagnet. Qualitatively this has already been reported for $ErRh_4B_4$ (sample with rectangular cross section) by Ott *et al.*[6] and for

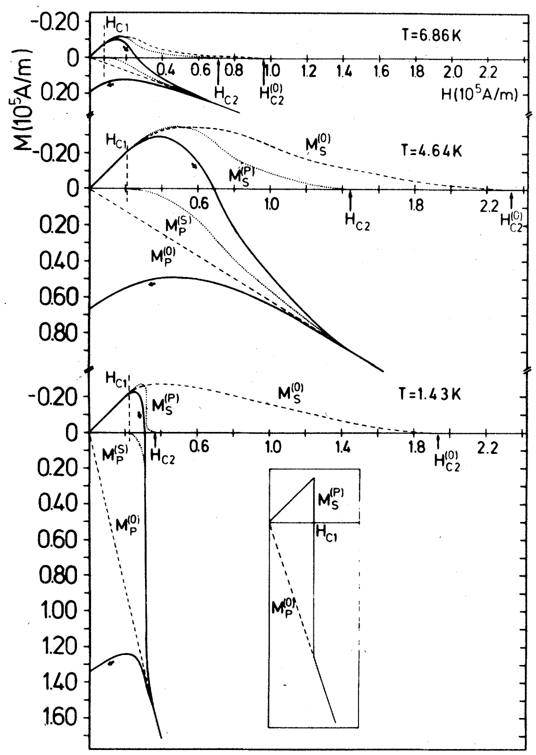

FIG. 1. Magnetization vs magnetic field for $Er_{0.73}Ho_{0.27}Rh_4B_4$ at 6.86 K (upper section), 4.64 K (middle section), and 1.43 K (lower section). The curves marked by arrows are from the experiment. The other curves are the uncoupled and coupled magnetizations of the superconducting and magnetic subsystem as defined in the text.

$Er_{0.60}Ho_{0.40}Rh_4B_4$ (spherical sample) by Ishikawa.[45] With decreasing temperature the influence of the paramagnetic magnetization increases. At 1.43 K the transition from the Meissner state to the normal state takes place within a very small field region. Furthermore, within the experimental error, the magnetization curve exhibits a vertical part. This behavior is not found if samples with large demagnetization factors [$N(\text{sphere})=\frac{1}{3}$] were used and no correction is applied.[45]

Except for the rounding, the magnetization at temperatures close to T_{c2} resembles the shape of a magnetic type-I superconductor, which is shown in the inset of Fig. 1. This transition from type-II to type-I behavior was theoretically predicted by Tachiki *et al.*[21] It seems that in the case of $ErRh_4B_4$ the transition from superconductivity to ferromagnetism is dominated not by pair-breaking effects due to exchange scattering and conduction-electron polarization, but by the macroscopic electromagnetic interactions between the superconducting system and the magnetic system. Therefore it is reasonable to analyze the magnetization curves according to a model similar to the mean-field theory of Jarić and Belić[26–28]: At $T_{c2} < T < T_{c1}$ the magnetic superconductor is considered to be composed of two subsystems, a usual type-II superconductor having a magnetization $M_s^{(0)}(H_{\text{ext}},T)$ and a paramagnet having a magnetization $M_p^{(0)}(H_{\text{ext}},T)$, if there were no coupling between them. Due to the coupling the magnetizations are changed to $M_s^{(p)}(H_{\text{ext}},T)$ for the superconductor and $M_p^{(s)}(H_{\text{ext}},T)$ for the paramagnet, with

$$M(H_{\text{ext}})=M_s^{(p)}(H_{\text{ext}})+M_p^{(s)}(H_{\text{ext}}) \tag{1}$$

In this model the interaction between the two subsystems is taken into account by a mutual modification of the effective field. The magnetic fields acting on the superconductor and paramagnet, respectively, are given by

$$H_{\text{ext},s}=H_{\text{ext}}+M_p^{(s)}(H_{\text{ext}}) \ , \tag{2}$$
$$H_{\text{ext},p}=H_{\text{ext}}+M_s^{(p)}(H_{\text{ext}}) \ .$$

Therefore

$$M_s^{(p)}(H_{\text{ext}})=M_s^{(0)}(H_{\text{ext},s}) \ , \tag{3}$$
$$M_p^{(s)}(H_{\text{ext}})=M_p^{(0)}(H_{\text{ext},p}) \ .$$

Furthermore the magnetization curves for $H_{\text{ext}} > H_{c2}$ show that at all temperatures H_{c2} is situated in the approximately linear part of the Brillouin function, which describes the magnetization of the paramagnet. This is also expected if one compares $H_{c2}(< 1.8\times10^5$ A/m in all cases) with the saturation magnetization $M_{p,\text{sat}}=8\times10^5$ A/m. Therefore, for

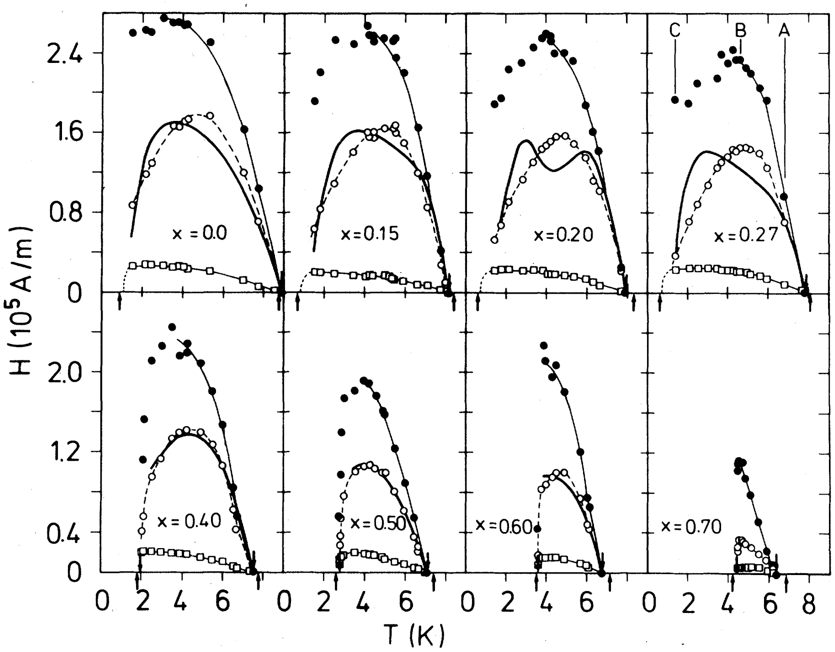

FIG. 2. H_{c1} (open squares), H_{c2} (open circles), and $H_{c2}^{(0)}$ (full circles) as function of temperature for $Er_{1-x}Ho_xRh_4B_4$. The heavy lines are fits according to Eq. (6). The arrows pointing upward indicate T_{c1} and T_{c2} from Ref. 39. The arrows pointing downward indicate T_{c1} and T_{c2} of this work. The letters A, B, and C mark the data points which correspond to the three magnetization curves of Fig. 1. The thin lines are drawn as guides to the eye.

$H_{ext} < H_{c2}, M_p^{(0)}$ is given by

$$M_p^{(0)}(H_{ext}, T) = \chi(T) H_{ext} \tag{4}$$

with $\chi(T) = M(H_{c2}(T))/H_{c2}(T)$, independent of $H_{ext,p}$.

From Eqs. (1)–(4) $M_s^{(0)}$, $M_s^{(p)}$, $M_p^{(0)}$, and $M_p^{(s)}$ can be calculated. Typical results are shown in Fig. 1. As expected, in the coupled system there is no contribution from the paramagnetic magnetization below H_{c1} and no contribution from the superconducting magnetization above H_{c2}. The calculation shows, that the superconducting subsystem itself $[M_s^{(0)}]$ remains type II even at low temperatures, where the coupled superconducting magnetization $[M_s^{(p)}]$ shows type-I character. In the model outlined above the upper critical field of the superconducting subsystem $H_{c2}^{(0)}(T)$, where $M_s^{(0)}(T)$ becomes zero, is given by

$$H_{c2}^{(0)}(T) = H_{c2}(T) + M(H_{c2}(T)) \ . \tag{5}$$

The dependence of H_{c1}, H_{c2}, and $H_{c2}^{(0)}$ on temperature and composition parameter x is shown in Fig. 2. H_{c1} increases slowly when the temperature is decreased below T_{c1}, but drops to zero within a very small temperature range (< 0.2 K) upon approaching T_{c2}. This was found for all samples, which had T_{c2}'s within our experimental limit ($T \geq 1.4$ K). Contrary to this, H_{c2} shows a bell-shaped behavior. The temperature of the H_{c2} maximum is 4.7 ± 0.3 K, almost independent of x. The T_{c1} and T_{c2} values of our samples differ slightly from those of Johnston *et al.*[39] For comparison their data are indicated in Fig. 2 by arrows pointing upward. For the samples with the lowest T_{c2}'s ($x = 0.15$, 0.20, and 0.27) (Ref. 39) the shape of the H_{c2} versus temperature curves is fairly symmetric. With increasing T_{c2} the low-temperature parts of the H_{c2} curves develop a pronounced anomaly: For $x \geq 0.40$ more than 50% of the H_{c2} increase occurs within a temperature interval of 0.4 K or less above T_{c2}. For $Er_{0.60}Ho_{0.40}Rh_4B_4$ this anomaly has been studied in detail by Ishikawa.[45] If the model of Jarić and Belić were sufficient to describe these magnetic superconductors, $H_{c2}^{(0)}(T)$ should have the temperature dependence of an orbital critical field. Figure 2 shows that this is apparently not the case.

The heavy lines in Fig. 2 are least-squares fits according to

$$H_{c2}(T) = Ah^*(T) - M(T) - BM^2(T) \ , \tag{6}$$

with $h^*(T)$ the reduced orbital field and $H_{c2}(T)$ and $M(T)$ taken from the experiment. The last term in Eq. 6 represents the spin-polarization effect which is proportional to the square of the magnetization.[45,46] Regarding all eight samples one has to conclude that the agreement for $x = 0.40$ and 0.50 is accidental.

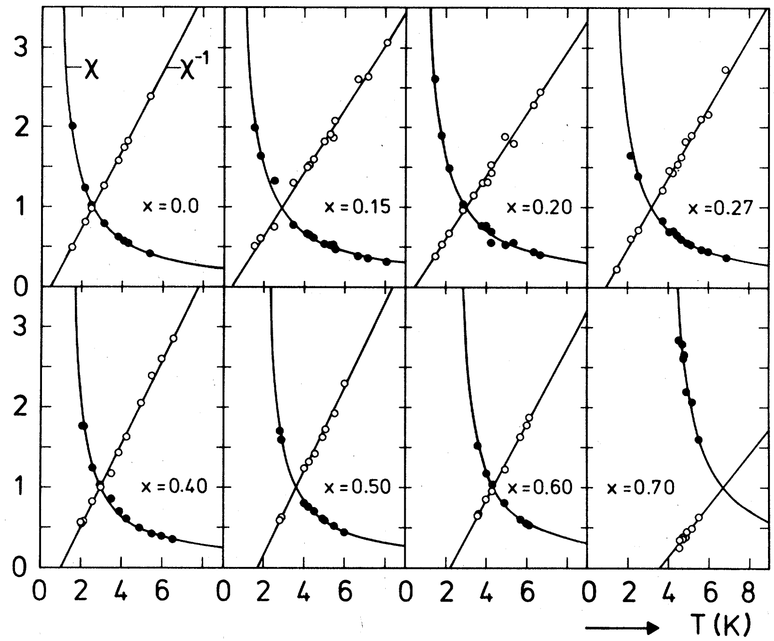

FIG. 3. Magnetic susceptibility and inverse magnetic susceptibility as function of temperature for $Er_{1-x}Ho_xRh_4B_4$. The lines are least-squares fits of Curie-Weiss laws to the data. For $x \geq 0.40$ the lowest-temperature point is taken just above T_{c2}.

It is interesting to point out two more features in Fig. 2: The maximum of $H_{c2}(T)$ decreases gradually from 1.8×10^5 to 1.0×10^5 A/m when x is increased from 0 to 0.60, but is reduced to 0.35×10^5 A/m for $x=0.70$. Even more striking is the fact, that $(dH_{c2}/dT)/_{T=T_{c1}}$ is constant within the experimental error for $x\leq0.60$, but about a factor of 3 smaller for $x=0.70$. This latter finding has been predicted by Youngner and Machida.[33]

Above H_{c2} the normal-state magnetic susceptibility $\chi(T)$ can be calculated according to Eq. (4). The results are plotted in Fig. 3. For all compositions $\chi^{-1}(T)$ can be well fitted by a straight line down to the lowest temperatures measured. This means $\chi(T)$ follows a Curie-Weiss law with a positive Curie temperature Θ_C. We calculate the effective magnetic moment to $\mu_{\rm eff}=(10.0\pm1.2)\mu_B$, which is in agreement with the free-ion value ($9.6\mu_B$ for Er^{3+} and $10.6\mu_B$ for Ho^{3+}). This is in contradiction to neutron-diffraction experiments of $ErRh_4B_4$ by Moncton *et al.*[10] who found a magnetic moment of $5.6\mu_B$, but close to the value of $(8.3\pm0.2)\mu_B$ observed by Mössbauer spectroscopy.[13] Measurements of the low-field magnetic susceptibility[38] between 7 and 294 K could also be described by a Curie-Weiss law with an effective magnetic moment of $(9.62\pm0.15)\mu_B$. Figure 4 shows T_{c1}, T_{c2}, and Θ_C as function of the composition parameter x. For $x\geq0.40$ the ferromagnetic Curie temperature is significantly below T_{c2}. The destruction of superconductivity above the temperature where long-range ferromagnetic order is established could be due to ferromagnetic spin fluctuations[31] or critical magnetic scattering of conduction electrons.[16] For $x\leq0.27$, T_{c2} was outside our experimental range. Therefore we could not

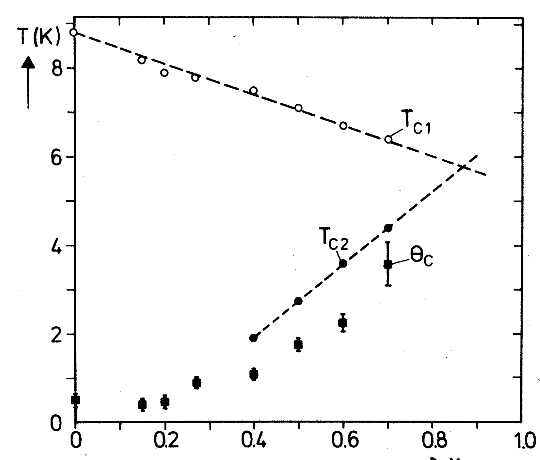

FIG. 4. T_{c1} (open circles), T_{c2} (full circles), and Θ_C (full squares) vs composition parameter x of $Er_{1-x}Ho_xRh_4B_4$. T_{c2} could not be measured for $x\leq0.27$ due to experimental limitations. For $x\geq0.40$ the Curie temperature Θ_C is significantly below T_{c2}.

clarify, whether T_{c2} and Θ_C coincide for smaller values of x, as it seems in Fig. 4. Johnston *et al.*[39] found a minimum in T_{c2} vs x near $x = 0.20$, which was attributed to a change in the orientation of the magnetic moments within the tetragonal unit cell from parallel to the tetragonal basal plane ($ErRh_4B_4$) to parallel to the c axis ($HoRh_4B_4$).[47] The orientation of the magnetic moments relative to the positions of the rhodium atoms, which are supposed to be responsible for superconductivity[22] could be of importance. The error in Θ_C, which is estimated to be less than 0.2 K for $x \leqslant 0.60$ and less than 0.5 K for $x = 0.70$, cannot account for the observed discrepancy.

Summarizing our results, we find:

(a) At temperatures close to T_{c2} the coupled superconducting magnetization $M_s^{(p)}$ shows typical features of a type-I superconductor. According to the model of Jarić and Belić the superconducting subsystem itself remains type II at all temperatures $T_{c2} < T < T_{c1}$.

(b) Macroscopic electromagnetic interaction between a superconducting and a magnetic subsystem seems to dominate the transition from superconductivity to ferromagnetism.

(c) $H_{c2}(T)$ shows an anomaly in a small temperature interval above T_{c2}, which becomes more pronounced with increasing T_{c2}.

(d) The maximum in $H_{c2}(T)$ decreases slowly with increasing x up to $x = 0.60$, but is reduced by a factor of 2 upon going from $x = 0.60$ to 0.70.

(e) $(dH_{c2}/dT)/_{T=T_{c1}}$ is constant for $x \leqslant 0.60$, but a factor of 3 smaller for $x = 0.70$.

(f) The magnetic susceptibility follows a Curie-Weiss law with a ferromagnetic Curie temperature Θ_C, which is significantly below T_{c2} for $x \geqslant 0.40$.

(g) Within the experimental error the effective magnetic moment is in accordance with the free-ion value.

ACKNOWLEDGMENTS

The authors acknowledge technical assistance by the Siemens Forschungslaboratorien in Erlangen. This work was supported by the Bundesministerium für Forschung and Technologie.

[1]Ø. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. 17, 21 (1975).
[2]R. N. Shelton, R. W. McCallum, and H. Adrian, Phys. Lett. A 56, 213 (1976).
[3]B. T. Matthias, E. Corenzwit, J. M. Vandenberg, and H. E. Barz, Proc. Natl. Acad. Sci. U.S.A. 74, 1334 (1977).
[4]J. M. Vandenberg and B. T. Matthias, Proc. Natl. Acad. Sci. U.S.A. 74, 1336 (1977).
[5]M. B. Maple, H. C. Hamaker, D. C. Johnston, H. B. MacKay, and L. D. Woolf, J. Less Common Met. 62, 251 (1978).
[6]H. R. Ott, W. A. Fertig, D. C. Johnston, M. B. Maple, and B. T. Matthias, J. Low Temp. Phys. 33, 159 (1978).
[7]L. D. Woolf, D. C. Johnston, H. B. MacKay, R. W. McCallum, and M. B. Maple, J. Low Temp. Phys. 35, 651 (1979).
[8]H. B. MacKay, L. D. Woolf, M. B. Maple, and D. C. Johnston, Phys. Rev. Lett. 42, 918 (1979).
[9]Ø. Fischer, M. Ishikawa, M. Pelizzone, and A. Treyvaud, J. Phys. (Paris) Colloq. 40, C5-89 (1979).
[10]D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 39, 1164 (1977).
[11]Y. Kuwasawa, L. Rinderer, and B. T. Matthias, J. Low Temp. Phys. 37, 179 (1979).
[12]D. E. Moncton, J. Appl. Phys. 50, 1880 (1979).
[13]G. K. Shenoy, B. D. Dunlop, F. Y. Fradin, C. W. Kimball, W. Potzel, F. Pröbst, and G. M. Kalvius, J. Appl. Phys. 50, 1872 (1979).
[14]D. E. Moncton, G. Shirane, and W. Thomlinson (unpublished).
[15]E. I. Blount and C. M. Varma, Phys. Rev. Lett. 42, 1079 (1979).
[16]A. Sakurai, Solid State Commun. 25, 867 (1978).
[17]S. Maekawa and M. Tachiki, Phys. Rev. B 18, 4688 (1978).
[18]H. Matsumoto, H. Umezawa, and M. Tachiki, Solid State Commun. 31, 157 (1979).
[19]M. Tachiki, A. Kotani, H. Matsumoto, and H. Umezawa, Solid State Commun. 31, 927 (1979).
[20]M. Tachiki, A. Kotani, H. Matsumoto, and H. Umezawa, Solid State Commun. 32, 599 (1979).
[21]M. Tachiki, H. Matsumoto, and H. Umezawa, Phys. Rev. B 20, 1915 (1979).
[22]T. Jarlborg, A. J. Freeman, and T. J. Watson-Yang, Phys. Rev. Lett. 39, 1032 (1977).
[23]A. J. Freemann and T. Jarlborg, J. Appl. Phys. 50, 1876 (1979).
[24]K. P. Sinha and P. Singh, J. Low Temp. Phys. 37, 389 (1979).
[25]M. A. Savchenko and A. V. Stefanovich, JETP Lett. 29, 118 (1979).
[26]M. V. Jarić and M. Belić, Phys. Rev. Lett. 42, 1015 (1979).
[27]M. V. Jarić, Phys. Rev. B 20, 4486 (1979).
[28]M. V. Jarić, Phys. Rev. B 22, 463 (1980).
[29]T. Lee, Y. A. Izyumov, and J. L. Birman, Phys. Rev. B 20, 4494 (1979).
[30]C. A. Balseiro and L. M. Falicov, Phys. Rev. B 19, 2548 (1979).
[31]K. Machida and D. Youngner, J. Low Temp. Phys. 35, 449 (1979).
[32]K. Machida and D. Youngner, J. Low Temp. Phys. 35, 561 (1979).
[33]D. Youngner and K. Machida, J. Low Temp. Phys. 36, 617 (1979).
[34]K. Machida, J. Low Temp. Phys. 37, 583 (1979).
[35]N. Grewe and B. Schuh, Z. Phys. B 36, 89 (1979).

[36]L. N. Bulaevski, A. I. Rusinov, and M. Kulić, Solid State Commun. 30, 59 (1979).
[37]M. Ishikawa and Ø. Fischer, Solid State Commun. 23, 37 (1977).
[38]W. A. Fertig, D. C. Johnston, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Matthias, Phys. Rev. Lett. 38, 987 (1977).
[39]D. C. Johnston, W. A. Fertig, M. B. Maple, and B. T. Matthias, Solid State Commun. 26, 141 (1978).
[40]R. N. Shelton, C. U. Segre, and D. C. Johnston, Solid State Commun. 33, 843 (1980).
[41]R. H. Wang, R. J. Laskowski, C. Y. Huang, J. L. Smith, and C. W. Chu, J. Appl. Phys. 49, 1392 (1978).
[42]C. Y. Huang, S. E. Kohn, S. Maekawa, and J. L. Smith, Solid State Commun. 32, 929 (1979).
[43]S. Kohn, R. H. Wang, J. L. Smith, and C. Y. Huang, J. Appl. Phys. 50, 1862 (1979).
[44]K. Okuda, Y. Nakakura, and K. Kadowaki, Solid State Commun. 32, 185 (1979).
[45]M. Ishikawa, Phys. Lett. A 74, 263 (1979).
[46]M. Ishikawa and Ø. Fischer, Solid State Commun. 24, 747 (1977).
[47]G. H. Lander, S. K. Sinha, and F. Y. Fradin, J. Appl. Phys. 50, 1990 (1979).