the energy levels of the Cu^{2+} ions can be well understood by the theory developed by Ham[9] and Druzhinin[10] which shows that

$$g_{ij}(E_k)=g_{ij}^{(0)}+\sum_k T_{ijk}E_k+\cdots,$$

$$A_{ij}(E_k)=A_{ij}^{(0)}+\sum_k Q_{ijk}E_k+\cdots,$$

where T_{ijk} and Q_{ijk} represent third-rank tensors describing the first-order change in the g and A tensors in the external field. The theory for the ferroelectric case still has to be developed and would apparently have to take into account the asymmetric shifts of the ions in the internal electric field and the change in the effective lattice force constants with temperature.

The "Stark" effect epr method thus seems to be particularly well suited for the study of lattice instabilities in displacive ferroelectrics. For Rochelle salt the present results demonstrate that it is the surrounding of the A sites which becomes unstable or disordered at the lower Curie point and that B sites are primarily affected at the higher Curie point.[8] The decrease of the anomalous polarizibility of the A sites for a particular direction of the applied field at the higher Curie point is probably a consequence of the disappearance of the spontaneous polarization field. The disappearance of the effect at low temperatures further shows that it is only the instability of the system connected with the ferroelectric transitions which makes the electric field shifts easily observable.

The authors are indebted to Mr. A. Levstik for the spontaneous polarization measurements.

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MAGNETIC MOMENT OF $ZrZn_2$ UP TO 150 kG: IS "PURE" $ZrZn_2$ FERROMAGNETIC?

S. Foner and E. J. McNiff, Jr.
National Magnet Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts

and

V. Sadagopan†‡
Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received 1 September 1967)

We present magnetic-moment measurements in polycrystalline and single-crystal $ZrZn_2$ for fields to 150 kG. The high-field susceptibility is identical for all materials whereas the low-field moment varies over a wide range. The data indicate that the low-field moment is correlated with trace impurities (such as Fe and Ti) and details of preparation. We suggest a localized-moment model for ferromagnetism in impure $ZrZn_2$ which is consistent with our results; but it is not yet clear whether or not "pure" $ZrZn_2$ is ferromagnetic.

An interesting feature of $ZrZn_2$ is that both Zr and Zn are nonmagnetic metals which are individually superconducting, yet the compound appears to be ferromagnetic. During the last decade numerous studies[1] in $ZrZn_2$ have been pursued particularly for evidence of itinerant electron ferromagnetism. In this Letter we present high-field magnetic-moment measurements which force us to re-examine the source of the ferromagnetism in the usual $ZrZn_2$ compounds and to inquire whether or not "pure" $ZrZn_2$ is ferromagnetic at all. The results are of direct interest to currently active studies of the theories of band magnetism, dilute alloys, localized moments, and exchange enhancement. Our high-field magnetic-moment data in polycrystalline and single-crystal $ZrZn_2$ up to 150 kG show the following: (1) $\sigma(0)$, the magnitude of the moment σ (in units of emu/g) extrapolated to $B=0$ from high field, varies over an extremely wide range and depends on such factors as method of sample preparation and impurities; (2) the high-field susceptibility $\chi_{HF}=\partial\sigma/\partial B$ (evaluated between 100 and 150 kG) does not vary appreciably from sample to sample despite the large $\sigma(0)$ variation; (3) there is a correlation between certain trace impurities and the magnitude of $\sigma(0)$. We conclude that earlier low-field moment and neutron-diffraction data[2] in (impure) $ZrZn_2$ do not clearly indicate whether or not "pure" $ZrZn_2$ is an intrinsic ferromagnet.[3]

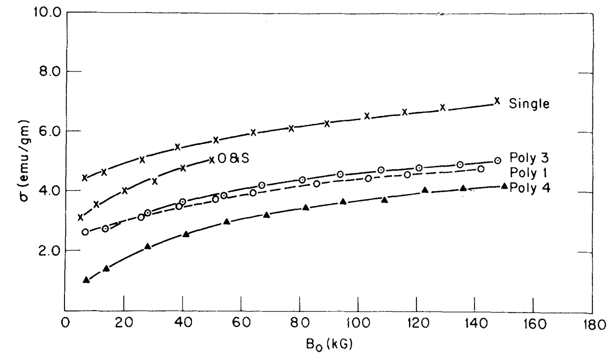

FIG. 1. Comparison of magnetic moment σ versus applied field B_0 at 4.2°K for various $ZrZn_2$ materials. "Single," single crystal $ZrZn_2$; "O & S," Ogawa and Sakamoto (Ref. 1); "Poly *X*," polycrystalline $ZrZn_2$ sample No. *X*. Note.—Poly 4 is not ferromagnetic at 4.2°K (see Table I).

Our magnetic-moment measurements to 150 kG at 4.2°K are shown in Fig. 1 for several polycrystalline $ZrZn_2$ materials[4] along with the high-field data of Ogawa and Sakamoto.[1] The measurements employ a very low-frequency vibrating-sample magnetometer[5] which time-averages the small field fluctuations present in the water-cooled high-power dc solenoids. Several features are noteworthy. First, σ is a nonlinear function of H even at highest fields; a decrease by a factor 3 in χ_{HF} occurs from 50 to 150 kG. Second, $\sigma(0)$ for different samples varies over a wide range. Third, the value of $\chi_{HF}(150\text{ kG})$ for all materials studied is identical (within ±10%), indicating that χ_{HF} is directly dependent on the bulk properties (cf. Table I). Fourth, the value of σ at any H depends on the manner of sample preparation. The magnitude of σ at low or high fields does not appear to be simply related to the bulk properties. Fifth, the value of χ_{HF} is larger than that reported[6] for paramagnetic Pd. Measurements to 1.3°K at high fields showed that the temperature dependence of χ_{HF} was quite small.

The single crystal[7] data (Fig. 2) demonstrate that χ_{HF} data in all the materials are identical within experimental error, independent of $\sigma(0)$, and reflect the bulk properties of the $ZrZn_2$, and that any low-field effects of paramagnetic impurities, domains, anisotropy, and spin waves are effectively suppressed. The nonlinear variation at high fields, as well as the large value of χ_{HF}, is consistent with the expected behavior for itinerant ferromagnetism with a small exchange splitting of the bands.[8] All of these features are bulk proper-

Table I. Selected impurity and magnetic data for $ZrZn_2$ samples.

	Impurity content estimated[a] from mass spectrometry (ppm at.)										Second phase[d]
Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Ta	σ_0[b]	$\chi_{HF}(150\text{ kG})$[c]	(% $ZrZn_3$)
Single crystal	5.3×10^3	50	145	2	370	2	16	21×10^3	4.2	9	5
Poly 3	190	160	170	59	1080	2	100	<0.5	2.2	10	5
Poly 4	65	2	180	17	270	4	44	2	4.2°K > T_c	11	10

[a] The absolute values are estimated to be accurate within a factor 3. The ratio of the relative impurities of Poly 3 and Poly 4 can be scaled since both were polycrystalline powders mixed with graphite for spark analysis. They may not be scaled directly with the single crystal which was sparked directly (see Ref. 9).

[b] σ_0(emu/g) is determined from the intercept at $B=0$ of a σ^2 vs B/σ plot.

[c] $\chi_{HF}(150\text{ kG})=\partial\sigma/\partial B$, the high-field susceptibility at 150 kG in units of 10^{-6} emu/g.

[d] Estimated from x-ray powder-pattern data.

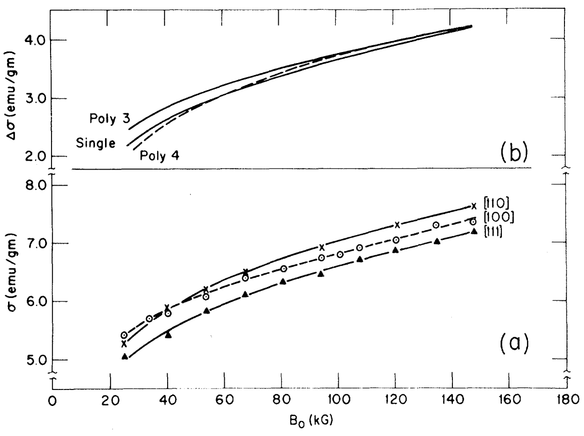

FIG. 2. Magnetic moment versus applied field. (a) Compares σ along principal axes for single crystal $ZrZn_2$. (b) Compares data in Fig. 1 for three materials. Note here that all data in Fig. 1 are displaced until the 148-kG points are coincident. The differential changes in σ, $\Delta\sigma$, are then plotted (on the same scale) with respect to this normalized high-field point to show the closely similar behavior of the high-field moment. The scatter in absolute value of σ for various orientations is within experimental error and includes the irregular sample geometry. The relative change in σ, from which χ_{HF} is determined, has a much smaller error.

ties of $ZrZn_2$. (Various aspects of the itinerant ferromagnetism will be discussed at a later time.) Furthermore, the close agreement of χ_{HF} for various materials shows that this quantity does not depend strongly on trace impurities. The spontaneous and low-field σ certainly do not reflect the "pure" $ZrZn_2$ properties since then the values of σ should be closely identical, which is clearly not the case. The absolute values of $\sigma(H)$ or χ in this region are therefore not directly useful for studies of "pure" $ZrZn_2$.

Our polycrystalline $ZrZn_2$ was made from powdered, nominally 99.9% Zr and semiconductor-grade Zn supplied by Leytess Metals Corporation of New York. The powders were mixed, cold pressed, and sintered for 24 h between 950 and 1000°C in evacuated quartz tubes. Optimum processing variables were determined empirically in order to minimize other phases. Attempts to introduce large percentages of Fe demonstrated very limited solubility; instead, an increased yield of $ZrZn_3$ was attained. (A limited Fe solubility would explain the fact that T_c does not exceed 35°K for $ZrZn_2$.) The apparently limited Fe solubility in $ZrZn_2$ has severely limited further examination of effects of impurities. We have examined three samples by spark mass spectrometry[9] for selected 3*d* impurities listed in Table I. Table I and Figs. 1 and 2 show a striking correlation—materials with high Fe and Ti[10] have a high σ.

Doniach and Wohlfarth[11] find that the giant moment of Fe in Pd scales as 1 μ_B per 10^{-6} emu/g of the Pd matrix susceptibility. Comparison with the large χ of $ZrZn_2$ at low fields suggests 50 μ_B or more per localized impurity (0.1 μ_B per $ZrZn_2$ molecule for 1500 ppm atomic Fe or Ti if Fe or Ti forms a localized moment). Although these estimates of a localized-moment source of ferromagnetism in $ZrZn_2$ are in agreement with the present limits of analysis (Table I), it is obvious that quantitative statements, here and concerning "pure" $ZrZn_2$, await detailed quantitative analysis of trace impurities in $ZrZn_2$.

A plot of σ^2 vs B/σ for the high-field Poly 4 data is almost linear with an intercept indicating that T_c for this sample is below 4.2°K (Table I). According to the analysis in Table I, Poly 4 is the most pure. It thus appears that pure $ZrZn_2$ may be nonferromagnetic and that the usual (impure) $ZrZn_2$ may be an extrinsic ferromagnet. We also note here that the most strongly ferromagnetic (single-crystal) $ZrZn_2$ is the most impure in all respects with an extremely large amount of Ti and Ta. Although we have not yet obtained sufficiently precise measures of the trace impurities to determine unambiguously the source of the low-field moment, it appears that impurities play a dominant role here.

Based on the present work, we seen that high-field susceptibility measurements permit discrimination between bulk and impurity effects. Ferromagnetic materials with large values of χ_{HF} must be closely examined in the "ultrapure" state in order to ascertain whether or not they are extrinsic or intrinsic ferromagnets.

In conclusion, several definitive tests are suggested to determine whether $ZrZn_2$ is an extrinsic or intrinsic ferromagnet: Ultrapure Zr may be used to fabricate pure $ZrZn_2$ in order to re-examine[12] $\sigma(H,T)$; a search for localized moments in impure $ZrZn_2$ may be made with Mössbauer[12] or nmr techniques; or the distribution of spin densities about impurities in $ZrZn_2$ may be examined by neutron-diffraction studies.[13] The results of these studies are expected in the near future. A detailed discussion of the magnetic properties of $ZrZn_2$ and related materials as a function of field, temperature, and purity will be presented in a future publication.

We are grateful to Dr. D. J. Kim and Dr. B. B. Schwartz for numerous valuable suggestions and comments during the course of this investigation, and to Mr. R. Doclo for assistance with valuable low-field data, to Professor C. G. Shull and Dr. R. R. Nathans for discussions concerning previous neutron-diffraction experiments, to Dr. S. C. Abrahams of Bell Telephone Laboratories for various single-crystal $ZrZn_2$ samples and discussions, to Dr. Maynard P. Hunt of the U. S. Air Force Cambridge Research Laboratory for spark mass-spectrographic analysis, to Professor W. H. Dennen for spectrographic analysis, and to Mr. A. T. Greenslade for valuable technical assistance with experiments. We have also profited from private communications prior to publication from Proferror E. P. Wohlfarth concerning his work.

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*Supported by the U. S. Air Force Office of Scientific Research.

†Work supported by a grant from National Aeronautics and Space Administration.

‡Now at Avco Research Laboratory, Everett, Massachusetts 02149.

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MODIFICATION OF THE UPPER CRITICAL FIELD IN A TWO-BAND SUPERCONDUCTOR

Victor K. Wong* and C. C. Sung†
Department of Physics, The Ohio State University, Columbus, Ohio

(Received 9 October 1967)

The upper critical field H_{c2} for a Type-II two-band superconductor is investigated in the pure limit. Near T_c, H_{c2} is dominated by the s band, whereas the thermodynamic properties are determined by the d band. A modification to the Gor'kov theory is found for the ratio of $K_1(T)$ at $T=0$ and $T=T_c$. This result may explain the discrepancy between the one-band theory and experimental data.

The recent measurement[1] of the specific heat of superconducting transition metals indicates the existence of the two energy gaps caused by overlapping s and d bands. A simple extension of the BCS theory to superconductors with overlapping bands is given by Suhl, Matthias, and Walker,[2] which is referred to as the two-band model. The experimental specific-heat data can be fitted in the two-band model with proper choices of the parameters.[3] Because of the high density of states of the d band, the thermodynamic properties near the critical temperature T_c of the two-band model are dominated by the d band; whereas the transport properties (e.g., electromagnetic properties and thermal conductivity) are dominated by