# Spin-flip Raman scattering in $KTaO_3$: Donors

K. Douglas and J. F. Scott
*Department of Physics, University of Colorado, Boulder, Colorado 80309*
(Received 22 February 1983; revised manuscript received 6 March 1984)

We have observed spin-flip scattering of laser light in crystals of potassium tantalate in magnetic fields from 4 to 12 T. This scattering is unobservably weak for excitation in the visible but becomes intense for uv excitation, due to the effects of resonance. The samples employed are $n$ type and weakly conducting at room temperature (0.5 $\Omega$ cm). At $T=1.8$ K they yield two spin-flip transitions having slightly anisotropic gyromagnetic ratios; we find, with an experimental uncertainty of $\pm 2\%$, $g_1=2.10$ and $g_2=4.4$, and zero-field splitting $2D \approx 2$ cm$^{-1}$; these transitions are compatible with assignment as $Ni^{3+}$ and $Fe^{3+}$ or $Ni^{2+}$, and both nickel and iron appear at concentrations of $\lesssim 300$ ppm in the specimens which exhibit spin-flip spectra.

## INTRODUCTION

Studies of spin-flip scattering in wide-band-gap semiconductors[1-5] have revealed a considerable amount of new information. This is especially true in cubic $p$-type materials with degenerate valence bands,[6-10] for which internal strains normally broaden inhomogeneously EPR spectra of holes beyond the level of detection.[11] The $ABO_3$ perovskites such as $KTaO_3$ and $SrTiO_3$ have degenerate $d$-like conduction bands with heavy and light electrons, which are similar qualitatively to the valence bands of II-VI compound semiconductors.[12] For that reason we believed that it would be possible to obtain information concerning their electron gyromagnetic values through spin-flip Raman scattering which is not readily available from other techniques. Measurement of gyromagnetic ratios ($g$ values) is one of the most sensitive tests of band-structure calculations.

However, spin-flip scattering in wide-band-gap materials is often dominated by donor and acceptor transitions rather than those of free carriers.[1,4,5,8-10] This can occur for several reasons: In $n$-type specimens of moderate carrier concentrations, the majority of the conduction electrons freeze out at low temperatures, leaving only donor transitions with sufficient intensity for detection; alternatively, in $p$-type materials or other semiconductors with degenerate conduction bands (such as $KTaO_3$, where the conduction band is $d$ like and originates from Ta orbitals) the spin-orbit coupling produces for $H \neq 0$ Landau levels of extremely irregular spacing and wave-vector dependences $E(q)$. This is shown very clearly in Fig. 6 of Hollis[6] for ZnTe. For carrier concentrations of $10^{17}$–$10^{18}$ cm$^{-3}$, many orbital levels will intersect the Fermi surface, and each will have a spin splitting of complicated $q$ dependence. In such a system the free-carrier spin-flip spectrum will be proportional to a complex density of states obtained by integrating from 0 to $k_F$. The integrated intensity may be greater than that for donor or acceptor scattering, but the spectrum will consist of broad continua rather than sharp peaks; and peak heights and experimental detectability will be worse than for impurity states, which are delta-function-like in energy. This has been well illustrated in Refs. 6 and 7 (see Fig. 5 of Hollis and Scott[6]).

Thus in a system such as $KTaO_3$ with a degenerate conduction band, donor scattering might be expected to dominate the spin-flip spectra, even though carriers are known not to freeze out and nominally pure samples were utilized. For this reason in our study, samples from three different sources were chosen. As discussed below, samples from Massachusetts Institute of Technology (MIT) and University of Tsukuba (UTS), Japan, yielded no observable spin-flip spectra, whereas specimens from the National Bureau of Standards (NBS) yielded very strong scattering we interpret as spin flip of electrons bound to Ni or Fe donors.

All of our attempts on $SrTiO_3$ and $KTaO_3$ with visible laser excitation were unsuccessful. However, with illumination in the ultraviolet we observed strong spin-flip scattering in $KTaO_3$, to be reported below. This is due to resonance enhancement which occurs for laser excitation energies near the $KTaO_3$ direct band gap. This work is the first uv spin-flip study to be reported, to our knowledge. Extensions to be reported subsequently are studies of $SrTiO_3$ for both insulating and semiconducting (oxygen-deficient) specimens; $SrTiO_{3-x}$ is, of course, a well-known[13] example of a superconducting semiconductor at very low temperatures.

$KTaO_3$ is a semiconductor of particular interest. It has extremely large values of both dielectric constant and mobility at low temperatures. And the carriers do not exhibit freeze out at any temperature.[14,15] The combined effect of the latter characteristics is a surprisingly high conductivity ($2\times 10^4$ $\Omega^{-1}$cm$^{-1}$ at 4 K). Samples having $T$-independent carrier concentrations between $10^{17}$ and $10^{19}$ cm$^{-3}$ have been grown in several laboratories; the light carrier concentrations are for undoped specimens in which the conductivity is thought to be due to oxygen vacancies. The heavier carrier concentrations are typically for Mn- or Sr-doped material. In our work we employed samples from the Solid State Chemistry Group at the Institute for Materials Research, National Bureau of Standards; five specimens grown by W. S. Brower and provided to us by W. R. Hosler were used (designated KT-9 here and in Ref.

 

15). Each of these yielded intense spin-flip scattering. One specimen (KT-11) originally supplied by Dr. Hans Jensen, Department of Physics, MIT, was also studied; it has a higher carrier concentration and yielded no spin-flip spectra. A seventh sample was provided to us by Dr. H. Uwe, University of Tsukuba, Japan. It had carrier concentration of a few times $10^{18}$ $cm^{-3}$ and also yielded no spin-flip spectra.

The band structure of $KTaO_3$ has been a source of some debate over the years. Kahn and Leyendecker made[16] a tight-binding model which predicted that the conduction band should have a many-valley structure similar to that in Si, whereas Matthiess used[12] an augmented-plane-wave calculation to predict a direct gap. Both Shubnikov–de Haas measurements[17] and Raman scattering[18] (assigned as transitions between spin-orbit-split conduction bands) favor the direct-gap picture. We hoped to measure gyromagnetic ratios for light and heavy electrons in the present work and to thereby test these models, but in fact, our data can best be interpreted in terms of Ni or Fe impurities. However, the strong resonant enhancement in cross sections for $\lambda_L \approx 350$ nm is in itself evidence for a direct gap in $KTaO_3$ at that wavelength.[12] Indirect-gap materials (such as GaP or Si) have rather weak resonant Raman enhancements.

## EXPERIMENT

Several specimens of $KTaO_3$ were employed for the present study. The data reported below were all obtained with samples from W. R. Hosler at the National Bureau of Standards. Seven specimens were employed; the first five (KT-9) had room-temperature conductivities of approximately 0.5 $\Omega$ cm. All gave intense spin-flip spectra. Experiments on semiconducting specimens of $KTaO_3$ obtained from the University of Tsukuba, Japan,[19] and MIT (Ref. 20) were unsuccessful as mentioned above; the reason for this is discussed in the following sections. The crystals used were typically $3\times4\times5$ $mm^3$ in size, undoped, colorless, and transparent; they were oriented by x-ray techniques to permit scattering geometries with the external magnetic field exactly along the [100], [110], or [111] directions. The magnet employed was a $Nb_3Sn$ tape-type design from Intermagnetics General. Its split-coil geometry permits scattering with momentum transfer in the $xy$ plane (horizontal in the laboratory frame) and field $H$ along $z$ (vertical). All experiments to be reported here were carried out in this geometry; that is, in the usual[21] notation, scattering was done in $x(yx)y$, $x(zz)y$, $x(zx)y$, and $x(yz)y$ configurations, where $z$ is the field direction and corresponds to [100], [110], and [111] sample directions. Fields between 4 and 12 T were employed, and the sample temperature was controlled to be 1.8 K; the specimens were immersed in superfluid pumped helium for all measurements. Detection and other details are described in Ref. 6.

Typical spectra are shown in Fig. 1. The observed linewidths are not instrumental; they are $\sim 2.0$ $cm^{-1}$, compared with a spectral resolution of about 1 $cm^{-1}$. The polarization of the observed lines was dominantly $zx$ and $yz$ polarizability tensor components, in agreement with the theoretical predictions of Yafet[22] for one-electron spin-flip processes. The scattering intensity was typically 200 counts/s with a time constant of 2.5 s, spectral-slit zero-field splittings of 0.1, 0.74, and 2.88 $cm^{-1}$ for different

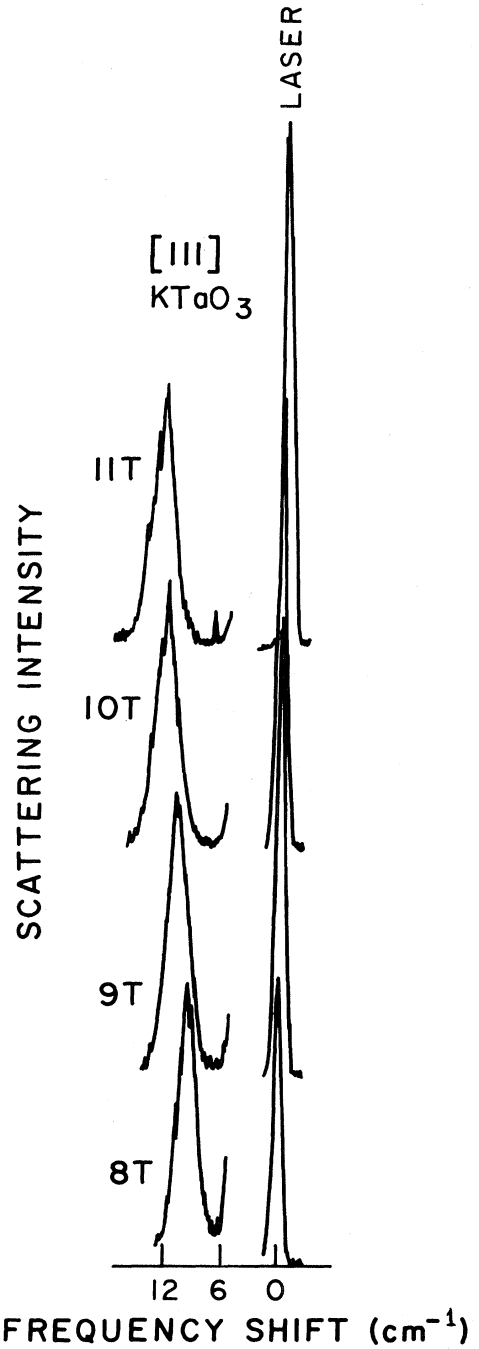


FIG. 1. A superposition of Raman data for $KTaO_3$ in magnetic fields of 8, 9, 10, and 11 T. This is for a "KT-9" sample cut to lie with [111] axis along the field $H$. Excitation was approximately 100 mW at 351.1 nm. Sample temperature was 1.85 K. Slit widths are 30 $\mu$m, time constant is 2.5 s, and the full scale ordinate is 1000 counts/s. The scattering geometry is $y(zy)x$, where $z$ is the direction of applied magnetic field (vertical in the laboratory frame). The observed linewidth of 2 $cm^{-1}$ is about twice the instrumental profile, which implies an intrinsic linewidth for the spin-flip process of about 1 $cm^{-1}$.

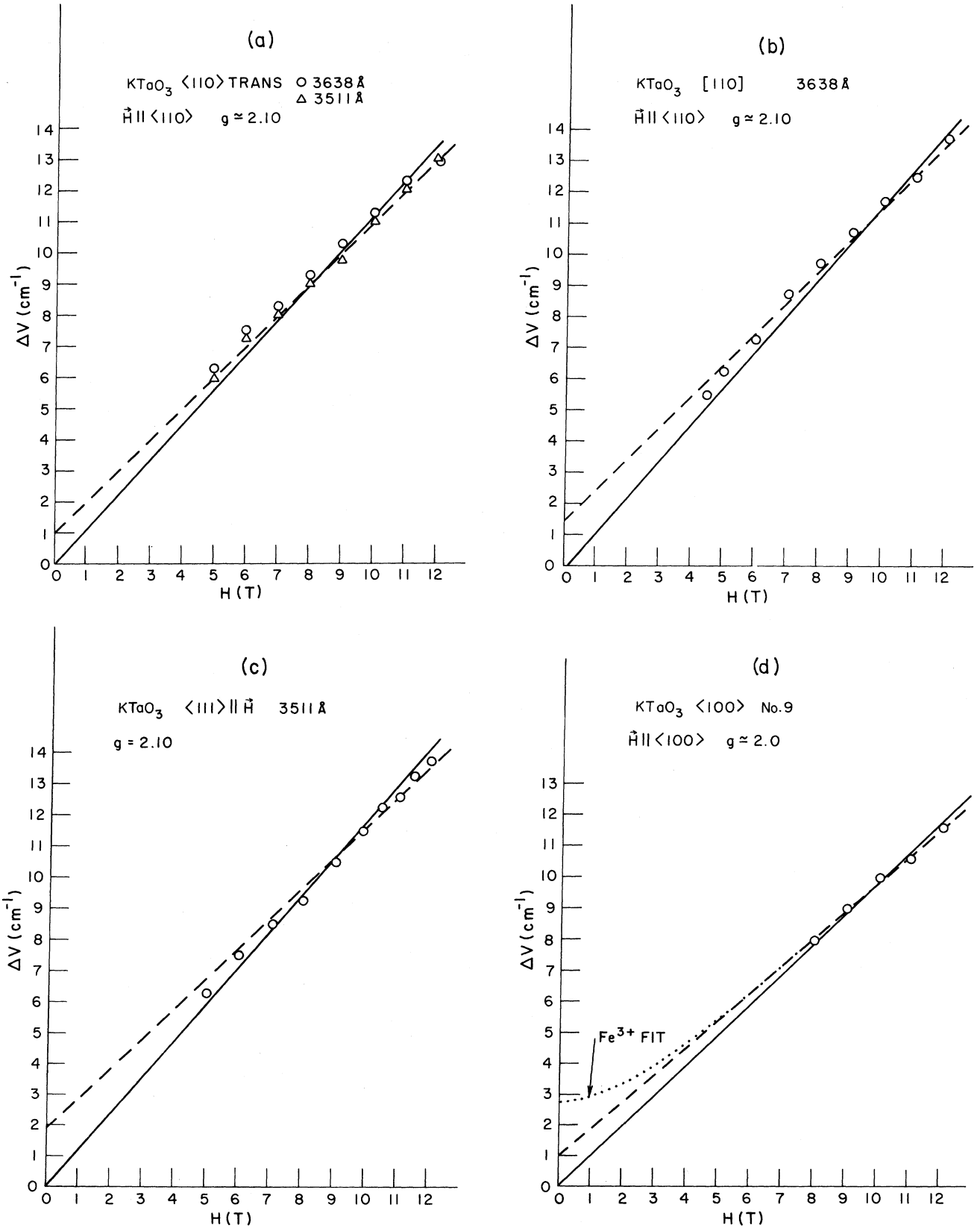


FIG. 2. Plots of peak position for spin-flip Raman transitions in $KTaO_3$ for "KT-9" specimens vs applied magnetic field. Solid line is best fit, assuming no zero-field splitting. Dashed curves in (a)—(c) assume $g=2.1$ (best fit to [110] data). Dotted curve in (d) assumes $Fe^{3+}$ parameters from Ref. 29. (a) $\vec{H}$|| [110] sample; KT-9 trans; (b) $\vec{H}$|| [110] sample KT-9; (c) $\vec{H}$|| [111]; (d) $\vec{H}$|| [100]. A fifth sample with $\vec{H}$|| [100] gave indistinguishable results from those in (d).

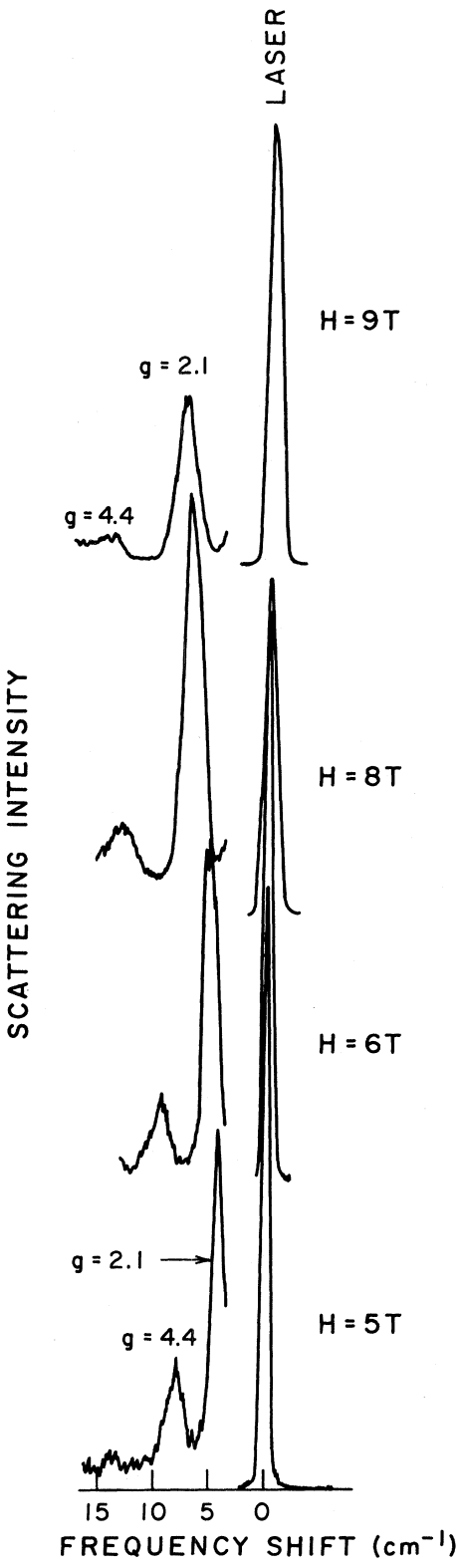


FIG. 3. $H=5$-, 6-, 8-, and 9-T field data for $KTaO_3$, showing spin-flip scattering for field along [110] and transitions at $g=2.1$ and 4.4. 400 mW at 351.1 nm. Other parameters as in Fig. 1. In an earlier preliminary analysis [Bull. Am. Phys. Soc. 28, 282 (1983)] we forced these data to a linear dependence $\omega=\mu_B gH$ with no zero-field energy. This yielded higher $g$ values (2.45) but a much worse fit of the data.

sites.[23–26] The zero-field splitting of $Ni^{2+}$ in $KTaO_3$ is not known, although its broad spectrum is seen in EPR; however, in other materials $Ni^{2+}$ has zero-field splitting[27] of about 2 $cm^{-1}$.

## ANALYSIS

Because our spectra were strongly sample dependent, they must be extrinsic. In Table I we list impurity content for impurities of greatest concentration, as measured by secondary-ion mass-spectroscopy (SIMS) analysis and by x-ray luminescence. All samples used show significant amounts of Na, Fe, Sn, and Ba. Two permitted quantiative measurement of Cr and Ni. The measurements to be in the (400—600)-ppm range. Note that the five samples which yielded spin-flip spectra do *not* have higher Fe or Ni concentrations than the two samples with no spin-flip spectra; however, the two samples with no spin-flip spectra had 30 to 300 times the Sn concentration of the others, and it seems likely to us that, at 1.8 K, this will signifi-

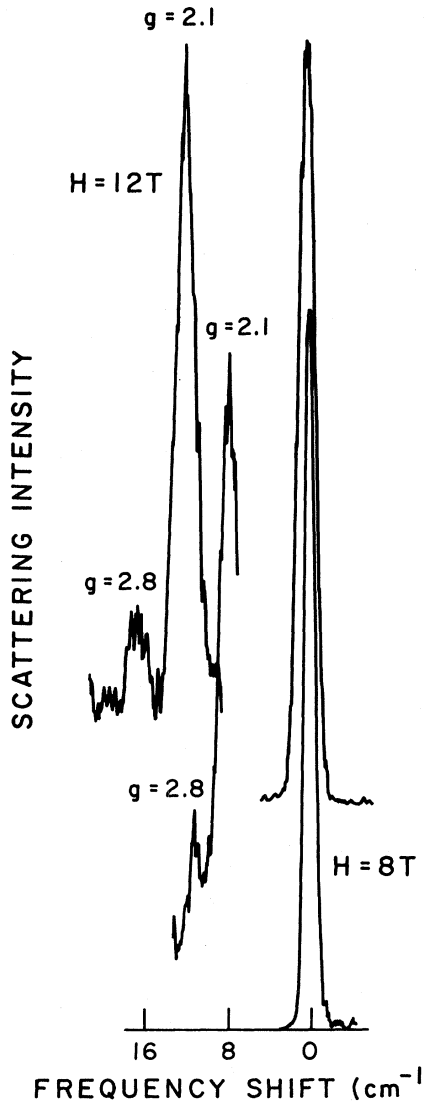


FIG. 4. $H=8$- and 12-T field data for $KTaO_3$, showing spin-flip scattering for field along [100] and transitions at $g=2.10$ and 2.8. 300 mW at 363.8 nm.

TABLE I. Impurity content of $KTaO_3$ specimens.

| Sample | SIMS Analysis[a] (relative %) depth profile Na | Fe | Sn | Ba | SIMS spectral analysis[b] $^{52}Cr$ | $^{60}Ni$ | X-ray luminescence | Spin-flip observed |
|---|---|---|---|---|---|---|---|---|
| MIT (KT-11) | 13.0 | 1.9 | 200.0 | 0.5 | 70 | 3 | | No |
| UTS (A-7) | 1.2 | 0.5 | 20.0 | 0.3 | | | | No |
| NBS (KT-9) | 1.0 | 1.0 | 1.0 | 1.0 | | | 400 ppm Ni | Yes |
| NBS (KT-9C) | 1.5 | 1.1 | 0.8 | 1.3 | | | 550 ppm Fe | Yes |
| NBS (9) | 0.4 | 0.1 | 0.5 | 0.4 | | | | Yes |
| NBS (trans) | 1.1 | 1.4 | 0.4 | 2.0 | 200 | 8 | | Yes |

[a]The SIMS study was done by John R. Dick III at the Solar Energy Institute, Golden, Colorado. No absolute percentages are given; the numbers for Na, Fe, Sn, and Ba are normalized to 1.0 for specimen KT-9 from NBS.

[b]Two samples yielded quantitative numbers for Cr and Ni. The numbers quoted from spectra analyses are counts/s and may be compared with $2\times10^5$ counts/s for $^{41}K$ isotopes in the same samples. This may be used to infer estimated absolute concentrations.

cantly influence the number of electrons localized at Fe or Ni sites. As discussed below, the observed gyromagnetic ratios and their isotropy agree with the EPR results[28] on $Ni^{3+}$, $Ni^{2+}$, and $Fe^{3+}$. $Fe^{3+}$ and $Ni^{3+}$ have been studied in $KTaO_3$ via EPR by Hannon[28] and by Wessel and Goldick.[29] $Ni^{2+}$ has been studied in the related perovskite $SrTiO_3$ by Rubins and Low,[30] where it was found to have an isotropic gyromagnetic ratio $g=2.20$. $Fe^{3+}$ is found in at least three sites:[28,29] one is cubic with $g=2.00$ and a small (0.1-$cm^{-1}$) zero-field splitting; the other two studied in detail are axial, presumed to involve oxygen vacancies, and have $g=2.00$ and large zero-field splittings[29] (2.88 and 0.74 $cm^{-1}$). The latter system yields an effective $g$ value of 4.25 between the $\pm\frac{1}{2}$, $S=\frac{5}{2}$ levels. $Ni^{3+}$ has[28] no zero-field splitting and anisotropic $g$ values: $g_{11}=2.2$, $g_1=2.1$ for the low-spin case ($Ta^{5+}$ octahedral sites); $g_{11}=2.2$, $g_1=4.4$ at the high-spin site (near $K^+$).

The data in Figs. 2(a)–2(d) can all be fit to a linear dependence with $g\simeq2.1$. If the fit is forced through the origin, systematic discrepancies become obvious, as shown. The linear fit with a finite zero-field splitting is better in each case; it yields an estimate of the zero-field splitting $\Delta\approx1.3$ $cm^{-1}$. However, this estimate is only a lower bound; if the terms add in quadrature,

$$\hbar\omega=(\Delta^2+\mu^2g^2H^2)^{1/2} \quad (1)$$

then $\Delta$ can be much larger. Figure 2(d) shows a fit to [100] data with the use of Eq. (1) and the $Fe^{3+}$ EPR parameters.[29] The data in Fig. 2 can be assigned, on the basis of $g$ values, to $Fe^{3+}$, $Ni^{3+}$, or $Ni^{2+}$. The existence of a probable zero-field splitting in Figs. 2(a)–2(c) would eliminate $Ni^{3+}$, but in the absence of $H=0$ data, this is not conclusive.

In Fig. 3 we see [110] data with a second spin-flip transition at $g=4.4$. It was observed in two samples with 10–30% the intensity of the $g=2.1$ line. Its $g$ value is compatible with either $Ni^{3+}$ at (or near) $K^+$ or axial $Fe^{3+}$. Finally, in Fig. 4 we see a weak additional line at $g=2.8$ whose origin is not understood.

In conclusion, all of our data are compatible with iron or nickel impurities. These were not intentional dopants. Both are known[28,29] to substitute for Ta and K and in the case of Ta to be associated with oxygen vacancies. These are donor states with strong axial fields.

## ACKNOWLEDGMENTS

Work supported by National Science Foundation Grant No. DMR-80-25238.

[1]D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968).
[2]P. A. Fleury and J. F. Scott, Phys. Rev. B 3, 1979 91971).
[3]J. F. Scott, T. C. Damen, and P. A. Fleury, Phys. Rev. B 6, 3856 (1972); E. Amzallag, C. Dugautier, P. Moch, and M. Balkanski, Solid State Commun. 12, 1303 (1973).
[4]L. L. Chase, W. Hayes, and J. F. Ryan, J. Phys. C 10, 2957 (1977).
[5]R. Romestain and S. Geschwind, in *Light Scattering in Solids,* edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 280; R. Romestain, S. Geschwind, and G. E. Devlin, Phys. Rev. Lett. 33, 10 (1974); 35, 803 (1975).
[6]R. L. Hollis and J. F. Scott, Phys. Rev. B 15, 942 (1977); R. L. Hollis, *ibid.* 15, 932 (1977).
[7]J. F. Scott, Rep. Prog. Phys. 43, 951 (1980).
[8]D. J. Toms, C. A. Helms, J. F. Scott, and S. Nakashima, Phys. Rev. B 18, 871 (1978); J. F. Scott, D. J. Toms, Le Si Dang, K. M. Lee, G. D. Watkins, and W. J. Choyke, *ibid.* 23, 2029 (1981).
[9]D. J. Toms, J. F. Scott, and S. Nakashima, Phys. Rev. B 19, 928 (1979).
[10]Y. Oka and M. Cardona, Phys. Rev. B 23, 4129 (1981).
[11]G. Feher, J. C. Hensel, and E. A. Gere, Phys. Rev. Lett. 5, 309 (1960).
[12]L. F. Matthiess, Phys. Rev. B 6, 4718 (1972).
[13]C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and

E. R. Pfeiffer, Phys. Rev. 163, 380 (1967).
[14]S. H. Wemple, Phys. Rev. 137, A1575 (1965).
[15]W. R. Hosler and H. P. R. Frederikse, Solid State Commun. 7, 1443 (1969).
[16]A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).
[17]H. Uwe, J. Kinoshita, K. Yoshihiro, C. Yamanouchi, and T. Sakudo, Phys. Rev. B 19, 3041 (1979); R. J. Nicholas, R. Kaplan, E. Kress, F. Kuchar, J. C. Ramage, R. A. Stradling, J. C. Portal, and S. Askenazy, in *Proceedings of the 14th International Conference on Semiconductors,* edited by B. L. H. Wilson (IOP, Edinburgh, 1978), p. 541.
[18]H. Uwe, K. Oka, H. Unoki, and T. Sakudo, in Proceedings of the 15th International Conference on Semiconductors, Kyoto, 1980, edited by S. Tanaka and Y. Toyozawa [J. Phys. Soc. Jpn., Suppl. A, 49, 577 (1980)].
[19]H. Uwe, Institute of Applied Physics, University of Tsukuba, Sakura, Ibaraki 305, Japan.
[20]A. Linz, Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
[21]T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 570 (1966).
[22]Y. Yafet, Phys. Rev. 152, 858 (1966).
[23]P. A. Wolff, Phys. Rev. 171, 436 (1968).
[24]R. L. Hollis and D. J. Toms (unpublished).
[25]K. Douglas, S. Nakashima, and J. F. Scott, Phys. Rev. B 28, 846 (1983); K. Douglas, J. F. Scott, and S. Nakashima, Bull. Am. Phys. Soc. 27, 13 (1982).
[26]D. D. Alov, S. S. Gubarev, V. B. Timofeev, and B. N. Shepel, Pis'ma Zh. Eksp. Teor. Fiz. 34, 76 (1981) [JETP Lett. 34, 71 (1981)]; A. K. Ramdas, Solid State Commun. 38, 365 (1981); Phys. Rev. Lett. 48, 1036 (1982); M. Nawrocki, R. Planel, G. Fishman, and R. Galazka, *ibid.* 46, 735 (1981).
[27]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), pp. 451–453.
[28]D. M. Hannon, Phys. Rev. 164, 366 (1967).
[29]G. Wessel and H. Goldick, J. Appl. Phys. 39, 4855 (1968).
[30]R. S. Rubins and W. Low, in *Paramagnetic Resonance,* edited by W. Low (Academic, New York, 1963), p. 59.